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Index in Water Distribution Systems

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IN
WATER DISTRIBUTION SYSTEMS

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

The study reported here focused upon one of the major problems of the water utility industry, i.e. delivering water to the consumer with the same quality as provided at the point of entry to the distribution system. Degradation of quality by reaction with the materials in the distribution system may lead to levels of contaminants greater than is desirable. Preventing this degradation will help the health and welfare of the consuming public.

Francis T. Mayo
Director
Water Engineering Research
Laboratory

ABSTRACT

Corrosion in water distribution systems was studied to gain a better understanding of the processes and to develop control strategies. Equations and calculation methods for determining the pH_s (or the theoretical pH at which the water is saturated with CaCO_3) were developed using a chemical model with and without ionic speciation. Several calculation procedures for determining pHs were analyzed and compared. Laboratory experiments using weight loss and electronic techniques for measuring corrosion rates were conducted in laboratory batch and continuously circulating systems using waters with different saturation indices, pH, alkalinity, chlorides, sulfates, chlorine residual, dissolved oxygen, organic color, calcium, buffer capacity and other water quality parameters. Changes in water quality were monitored in experiments with mild steel, galvanized steel and copper coupons. Corrosion products obtained from coupons exposed to continuously circulated solution were analyzed by wet chemical techniques and x-ray diffraction. Increases in dissolved oxygen, chlorides, sulfates, chlorine residual, and hydrogen ion concentration accelerated corrosion of metal specimens. Higher pH, calcium content, buffer capacity and organic color decreased the corrosion rate. A model was formulated which expresses corrosion rate in terms of chlorides, sulfates, alkalinity, dissolved oxygen, calcium, buffer capacity, saturation index, and immersion time. A four-variable corrosion rate model was developed from the multivariate analysis of corrosion data for mild steel in the batch studies. The model included total dissolved solids, dissolved oxygen, saturation index and exposure time. Results indicate Saturation Index cannot be used alone to indicate the extent of corrosion or to measure the corrosivity of a water.

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CONTENTS

Foreword.....	iii
Abstract.....	iv
Acknowledgments.....	viii
1. Introduction.....	1
2. Conclusions.....	3
3. Recommendations.....	4
4. Principles of Corrosion.....	5
Thermodynamic Aspects.....	6
Pourbaix Diagram.....	9
Kinetic Considerations and Corrosion Rates.....	11
5. Experimental Methods and Materials.....	13
Evaluation of CaCO_3 Saturation State.....	13
Laboratory Studies of Corrosion.....	13
Jar Tests.....	13
Loop Studies.....	16
Field Investigations.....	19
Chemical Analyses.....	19
Metallic Ions: Ca, Mg, Na, Zn, and Cu.....	19
Total Dissolved Iron.....	19
Chloride Sulfate.....	20
pH and Alkalinity.....	20
Dissolved Oxygen and Conductivity.....	20
Chlorine Residual Determination.....	20
Color Measurements.....	20
X-Ray Diffraction.....	21
6. Calcium Carbonate Saturation and Corrosivity Indices.....	22
7. Development of Alternative Calculation Methods for pHs...27	
Chemical Model of CaCO_3 Solubility Equilibrium.....	27
Derivation of Two New pHs Equations.....	29
Computational Procedure for Determining pHs.....	39

8. Results and Discussion.....	47
Studies on the pH of Calcium Carbonate Saturation.....	47
Evaluation of the pHs of the 155 Water Samples Using	
the Quadratic pHs formula.....	47
Extent of Ion Pair Formation.....	47
Effect of Water Quality Parameters on pHs.....	59
Statistical Models For Predicting the pH of	
CaCO ₃ Saturation.....	62
Comparison of the pHs Values Obtained from the Different	
Calculation Methods.....	69
Experimental Evaluation of the CaCO ₃ Saturation	
States of the Water Systems.....	83
Relationship of Saturation Index with Gibbs	
Free Energy Change.....	91
Corrosion Studies in Jar Systems.....	94
Mild Steel.....	94
Corrosive Behaviors of Waters with Different	
Saturation Indices.....	94
Effect of Calcium Concentration.....	103
Influence of Alkalinity, pH, and Buffer Capacity...	105
Acceleration of Corrosion due to Dissolved Oxygen...	117
Effects of Water Quality.....	119
Chlorine Residual.....	122
Natural Color.....	122
Effect of Specific Ions.....	124
Redox Potential.....	130
Variation in Water Quality.....	137
The Nature of Corrosion.....	139
Statistical Evaluation.....	149
Galvanized Steel.....	154
Corrosive Behavior of Five Waters with	
Different Saturation Indices.....	154
Effect of pH.....	157
Influence of Dissolved Oxygen.....	159
Effect of Water Quality.....	160
Effect of Chlorine Residual.....	160
Natural Color.....	164
Effect of Specific Ions.....	164
Redox Potential.....	169
Variation in Water Quality.....	169
The Nature of Corrosion.....	175

Copper.....	175
Effect of Water Quality.....	176
Effect of pH.....	179
Dissolved Oxygen.....	179
Chlorine Residual.....	185
Natural Color.....	186
Specific Ions.....	186
Redox Potential.....	192
Variation in Water Quality.....	199
The Nature of Corrosion.....	199
Corrosion Studies in Circulating System.....	203
Influence of Water Velocity on the Corrosion of Mild Steel.....	203
Corrosion of Black Steel Pipes in Waters with Different Saturation Indices.....	205
Changes in Water Quality During Corrosion of Steel Pipes.....	207
Analysis of Corrosion Products from Mild and Black Steel Pipes.....	211
Corrosion of Galvanized Steel in Circulating Waters with Different Saturation Indices.....	222
Water Quality Changes During Corrosion of Galvanized Steel.....	222
Analysis of Corrosion Products from Galvanized Steel.....	225
Field Investigations.....	231
Correlation of Corrosion Rate of Mild Steel with Saturation Index and Water Quality Parameters.....	236
9. Summary.....	247
References.....	248

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SECTION 1

INTRODUCTION

Corrosion of pipe in public water supply systems has been recognized as a serious problem since the beginning of the 20th century. In 1947, corrosion costs in the water industry were reported to be \$40 million per year (1). Recently the economic implications of corrosion have become a matter of increasing concern. Estimated replacement costs for U.S. community water systems damaged by corrosion range from \$17 billion (2) to \$75 billion (4,5). Thus, if corrosion problems continue unabated, an increasingly heavy financial burden will be imposed upon our society.

In addition to the economic consequences, the deterioration of metallic structures usually causes degradation of drinking water quality. The corrosion products also pose potential health risks. Consequently, the U.S. Environmental Protection Agency (EPA) has amended the National Interim Primary Drinking Water Regulations to require public water utilities carry out a corrosion monitoring control program. This program includes identification of the presence and sources of corrosion products, and the subsequent implementation of effective corrosion control measures.

A basic understanding of corrosion, (particularly internal corrosion of the water pipes) is important in launching a successful corrosion control program. But despite the great advances in recent years, our knowledge is still inadequate to control corrosion of metal pipes in contact with water containing dissolved chemicals. More information is needed to devise the best method for mitigating corrosion. And although several approaches can be used to control corrosion (6,7), only a few can be applied to drinking water systems because of economic or health constraints.

Formation of a CaCO_3 precipitate on the metal surface has been one of the better control strategies for combatting corrosion. One distinct advantage of this method is that the chemical ingredients required naturally occur in potable waters and are not considered hazardous to public health. For this reason the pH_s (or the pH of CaCO_3 saturation) is commonly determined in many water plants to ensure that the treated water protects sufficiently against corrosion. Unfortunately, most of these calculation methods (8,9) are not accurate enough and provide only an approximate value. Hence, a much more precise method of determining pH_s is needed. Likewise, the effects of important water quality parameters on pH_s and corrosion of metals used in the distribution systems need further study.

This investigation deals with the derivation of a more accurate theoretical expression for pH_s , a comparative analysis of other calculation methods for determining pH_s , development of a simplified method of predicting the exact pH_s accurately, evaluation of the corrosive behaviors of waters with different saturation indices, assessment of the effects of water quality factors on the corrosion rates of mild steel, galvanized steel, and copper, and analysis of the relationship between corrosion rate and water quality parameters.

SECTION 2

CONCLUSIONS

Two alternative equations can be used for determining the pH of CaCO_3 saturation (pH_s) of waters. A simpler method of calculating pH_s was found in which the pH_s is defined by a statistical predictive equation composed of a linear combination of the logarithms of total dissolved solids, total alkalinity, and analytical concentrations of calcium, magnesium, and sulfate. Comparison of eight calculation procedures for evaluating the pH_s of 155 water samples revealed that values obtained by using the two newly derived equations, the WATSPEC2 program, and the best four- and five-variable predictive equations are approximately equal. The values derived from Langelier's and Larson-Buswell formulae are lower than the pH_s values found in the other calculation procedures. The highest values are those from the graphical approximations using Caldwell-Lawrence diagrams.

The sign and magnitude of the saturation indices of waters used in the jar and loop studies were not directly related to the corrosion rate.

Dissolved oxygen was found to accelerate the corrosion rates of mild steel, black steel, galvanized steel, and copper. Likewise, acidic pH, chlorine residual, and increasing amounts of chlorides and sulfates increased corrosion rates of the same metals. Increase in calcium concentration, total alkalinity, and low water flow velocity retarded the corrosion of mild steel. Organic color, derived from a lake water, decreased the corrosion rates of mild steel and galvanized steel but enhanced the corrosion of copper. The corrosion products from mild steel and black steel pipes used in the loop studies were generally composed of goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), magnetite (Fe_3O_4) and calcite and aragonite (two forms of CaCO_3) irrespective of the saturation index of the water used. Both x-ray diffraction analysis and wet chemical analysis suggest that hydrozincite [$\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$], aragonite, and hematite (Fe_2O_3) were present in the corrosion products from galvanized steel pipes.

The corrosivity of water toward a metal cannot be evaluated simply in terms of the CaCO_3 saturation index alone. Multivariate analyses of the correlation between the corrosion rate of mild steel from batch studies and various water quality parameters revealed that the corrosion rate is best predicted by an expression involving four variables: total dissolved solids, dissolved oxygen, saturation index, and immersion time. An empirically constructed nonlinear corrosion rate model consisting of eight variables (chloride, sulfate, dissolved oxygen, alkalinity, calcium, buffer capacity, saturation index, and the exposure time of the metal to the solution) yielded satisfactory graphical fit to the experimental data.

SECTION 3

RECOMMENDATIONS

Additional experiments using a larger loop system will be required to expand the base of corrosion data from which meaningful conclusions can be drawn. This loop system should be studied under carefully controlled laboratory conditions where the temperature of the entire system can be regulated. Corrosion rates and water quality changes should be monitored in a program to test different metals over the temperature ranges occurring in utility systems. More field studies will be needed to evaluate more thoroughly how water quality factors affects corrosion and how corrosion affects water quality. The type and nature of plumbing materials but also the extent of metal leaching and quality of the finished water should all be considered. A computer correlation of all the corrosion data and relevant water quality records gathered from these studies should be made to develop a better model of the effect of water quality parameters on corrosion rates in distribution systems. Interaction between corrosion-promoting agents and corrosion-inhibiting factors ought to be considered in framing a more holistic approach for controlling internal corrosion.

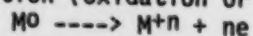
SECTION 4

PRINCIPLES OF CORROSION

Corrosion is commonly defined as the destructive action of a metal by electrochemical or chemical reaction with its environment. This destructive action is electrochemical in nature. Certain areas of the metal provide sites for oxidation and reduction reactions that eventually give rise to corrosion cells. The region where the oxidative half reaction takes place is called the anode and that where the reductive half reaction occurs is known as the cathode. One oxidation reaction usually takes place as shown in Table 1.

Table 1. General Redox Reactions at the Anode and Cathode

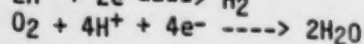
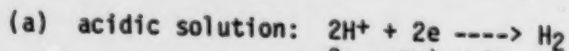
I. Anode reaction (oxidation or corrosion of metal M)



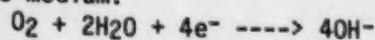
where n = charge

e = electron

II. Possible cathode reactions (reduction)



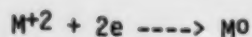
(b) neutral or alkaline medium:



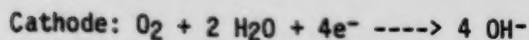
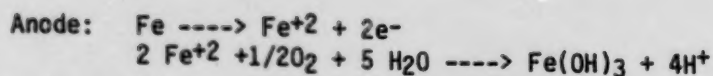
(c) metal ion reduction:



(d) metal plating:



Although different cathodic reactions can occur simultaneously on a corroding metal, hydrogen evolution, II(a), and oxygen reduction, II(b), are frequently the observed reduction processes. For corrosion of iron in an aqueous system containing dissolved oxygen, the following half reactions can take place



Corrosion in aqueous solution proceeds with the formation of corrosion cells that participate in the electrochemical processes. Although three general types are known (7), only two are often encountered in potable water systems. The first one is the dissimilar electrode cell which arises when two different metals are in direct contact. As a result of this contact and the difference in electrode potentials between two metals, a sufficient driving force exists to support oxidation in one of them and reduction in the other. Thus when iron and copper are connected to one another in contact with electrolyte solution, iron will undergo oxidation and corrode but copper will not have any corrosion damage. Another type of corrosion cell is triggered by the differences in chemical composition of the aqueous solution in contact with the metal. Localized differences in salt concentration gives rise to what is known as concentration cells. This can be exemplified by two copper electrodes, one in contact with dilute CuSO_4 solution, and the other in a more concentrated CuSO_4 solution. The tendency to balance the Cu^{2+} concentration is achieved by the anodic dissolution or corrosion of the copper electrode in the dilute solution and reduction of Cu^{2+} in the concentrated solution by consuming electrons to deposit elemental Cu .

Differential distribution of dissolved gases in the aqueous system could also provide impetus for corrosion. The difference in oxygen concentration between aerobic regions and essentially anaerobic areas of the metal can cause an electric current to flow and initiate corrosion. This type of cell is responsible for the localized corrosive attack often observed in crevices and pits when iron rusts. As shown in Figure 1, corrosion products covering the iron surface prevent O_2 from reaching the metal thereby forming anaerobic layer. The surface near the corrosion products has greater access to O_2 so that the formation of differential oxygen cells is greatly facilitated.

Thermodynamic Aspects

The tendency of a metal to corrode or be transformed into metal ions in a corrosive solution can be related to the free energy change of the electrochemical reaction involved. The relationship between Gibbs free energy change, ΔG , and electrode potential, E , is

$$\Delta G = nFE$$

where n = number of electrons involved in the reaction and F = Faraday constant. The relationship at standard conditions becomes

$$\Delta G^\circ = nFE^\circ$$

where ΔG° and E° denotes standard free energy change and standard electrode

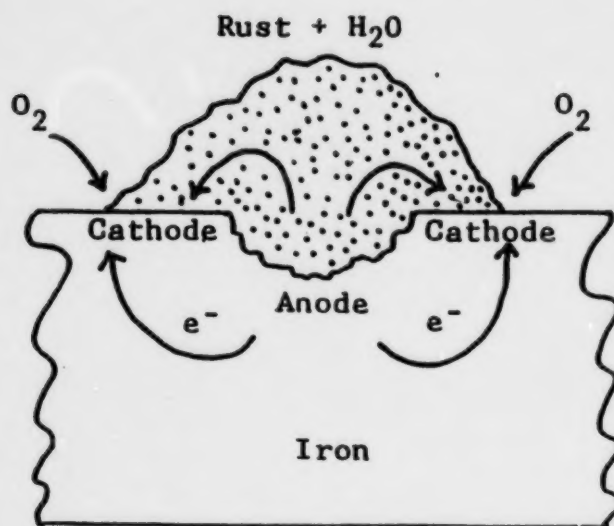


Figure 1. Pitting Due to Differential Oxygen Concentration Cells.

potential, respectively. The electrode potential for the half reaction

$$\text{Red} = \text{Ox} + ne$$

 can be written, using the Nernst equation, as

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]} \quad (1)$$

where E = electrode potential of the half reaction

E° = standard single electrode potential

n = number of electrons involved

R = universal gas constant

T = absolute temperature (°K)

F = Faradays constant

$[\text{Ox}]$ = concentration of oxidized species

$[\text{Red}]$ = concentration of reduced species

Using equation (1) for the oxidative half reaction at the anode and reductive half reaction at the cathode

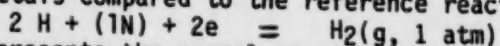
Anode: $\text{Ared} = \text{Aox} + ne$

Cathode: $\text{Cox} = ne + \text{Cred}$

the resulting equilibrium cell potential, E_{cell} , for the system becomes

$$E_{\text{cell}} = E_{\text{C}}^\circ - E_{\text{A}}^\circ + \frac{0.059}{n} \log \frac{[\text{Cox}][\text{Ared}]}{[\text{Cred}][\text{Aox}]} \quad (2)$$

after evaluating the constants at 25°C and transforming $\ln$ into $\log_{10}$. The letters a and c indicate the anode and cathode respectively. Typical standard electrode potential of some metals commonly encountered in water systems are presented in Table 2. The values are the electrode potentials of the metals compared to the reference reaction



which represents the normal or standard hydrogen electrode.

Table 2. Standard Electrode Reduction Potentials of Some Metals*

Reaction	E° , Volts
$\text{Zn}^{+2} + 2e^- = \text{Zn}$	-0.763
$\text{Cd}^{+2} + 2e^- = \text{Cd}$	-0.403
$\text{Fe}^{+2} + 2e^- = \text{Fe}$	-0.409
$\text{Fe}^{+3} + 3e^- = \text{Fe}$	-0.306
$\text{Fe}^{+3} + e^- = \text{Fe}^{+2} (1\text{ f HCl})^\dagger$	+0.770
$\text{Fe}^{+3} + e^- = \text{Fe}^{+2} (1\text{ f HClO}_4)$	+0.747
$\text{Fe}^{+3} + e^- = \text{Fe}^{+2} (0.5\text{ f H}_2\text{SO}_4)$	+0.679
$\text{Fe}^{+3} + e^- = \text{Fe}^{+2} (1\text{ f H}_3\text{PO}_4)$	+0.438
$\text{Cu}^+ + e^- = \text{Cu}$	+0.340
$\text{Cu}^{+2} + 2e^- = \text{Cu}$	+0.340

*Values taken from reference (10)

$\dagger$ refers to the formality of the solution.

Pourbaix Diagram

The effect of pH on the reversible electrode potentials of the anodic and cathodic reactions is also important in considering the thermodynamics of corrosion. The thermodynamic treatment of electrode potentials coupled with pH effects gives useful information as far as understanding and controlling corrosion is concerned. Pourbaix (11) has developed and popularized equilibrium potential - pH graphs which have become known as Pourbaix diagrams. These plots present the thermodynamic stability of a metal, regions of coexistence of metal ions and stable metal oxide or any other insoluble corrosion product. Construction of these diagrams requires information such as thermodynamic data associated with the equilibrium redox reactions and manipulation of appropriate Nernst equations. The procedure for the construction of Pourbaix diagrams is straightforward. Verink (12) has described a simplified procedure for constructing Pourbaix diagrams. Other computer-assisted calculations (13,14) and plotting techniques (15) are currently available.

A typical Pourbaix diagram for a metal-water system at 25° C and 1 atm. pressure is shown in Figure 2 for iron. The area between two broken lines (a and b) is the stability region of water. The areas above line "b" indicate that water is unstable with regard to the evolution of oxygen and, hence, represents water with a high dissolved oxygen content. Below line "a", water is unstable and reacts by hydrogen evolution and denotes very low oxygen content. Each line in the diagram indicates the conditions of thermodynamic equilibrium for a particular reaction. The line could be horizontal, vertical, or sloping. A horizontal line represents a reaction that is pH dependent, but does not include electron transfer. A vertical line involves electrons but not H^+ or OH^- . Both pH and electron transfer are involved for a sloping line. For instance, the sloping line "c" separating Fe^{+2} from Fe_2O_3 represents the reaction $2Fe^{+2} + 3H_2O \rightarrow Fe_2O_3 + 6H + 6e^-$. Another reaction that is affected by both electron transfer and pH is represented by line "d", which corresponds to the reaction $3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e^-$. The pH in the diagram refers to that of a solution in direct contact with the metal surface. In some cases, this pH value differs from that of the bulk solution.

One important use of a Pourbaix diagram is that it presents the theoretical equilibrium conditions under which corrosion is possible. Hence, we could deduce from Figure 2 that the area corresponding to the stability of soluble metallic species (Fe^{+2} , Fe^{+3}) represents corrosion. Regions where metal oxides (Fe_2O_3 , Fe_3O_4) are stable will indicate passivation, that is, corrosion is prevented as a result of a continuous coherent oxide film that coats the metal surface. At lower electrode potential values, the reaction of metallic ions with electrons is energetically favored. Therefore, the metal is stable in this area and is said to be immune to corrosion.

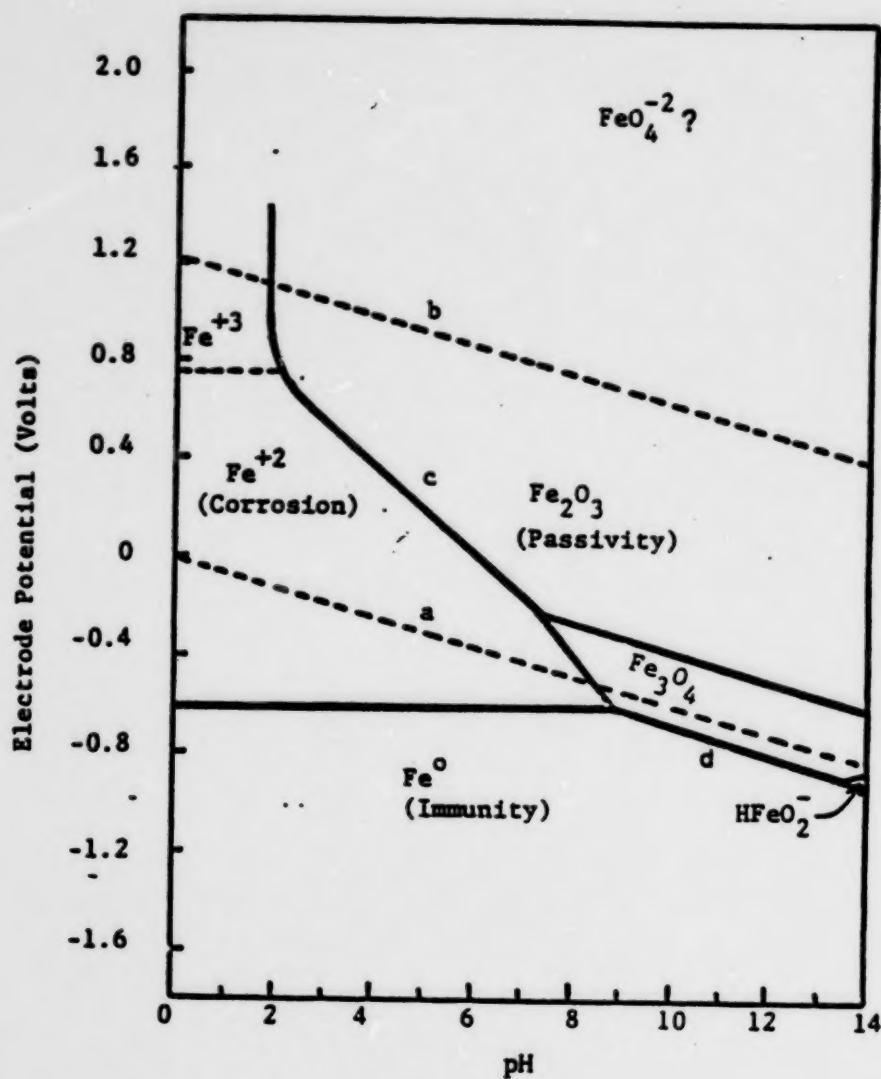


Figure 2. Potential -pH Equilibrium Diagram for the Iron-Water System at 25°C. Plot was Constructed by Considering As Solid Substances Only Fe, Fe_2O_3 and Fe_3O_4 with $[\text{Fe}^{+3}]$ and $[\text{Fe}^{+2}] = 10^{-6}$ M.

Kinetic considerations and corrosion rates

Information from the thermodynamic treatment of corrosion and Pourbaix diagrams can be complemented by kinetic analysis of the electrochemical dissolution of metals to provide a better understanding of corrosion processes. A fundamental expression of electrochemical kinetics which relates the reaction rate at the metal surface to the current density and electrode potential is the Butler equation

$$i = i_0 \left[\exp \left(\frac{\alpha F}{RT} \right) \eta - \exp \left(- \frac{(1 - \alpha) F}{RT} \eta \right) \right] \quad (3)$$

where i = polarization current density

i_0 = exchange current density

α = charge transfer coefficient

η = polarization overvoltage

F, R, T = are as defined previously

The overvoltage, η , is a measure of the perturbation from equilibrium and is defined as

$$\eta = E_{\phi_i} - E_{\phi}$$

where E_{ϕ} = single electrode potential with an impressed current i flowing through the cell

E_{ϕ} = single electrode potential without external current flowing

Equation (3), nevertheless, is only valid for a simple redox process where a single electron transfer with no other chemical reactions involved. Hence to increase the utility of the equation, it was modified and simplified to be useful in evaluating corrosion rates. The resulting expression becomes

$$i_{\text{corr}} = \frac{1}{2.3} \left(\frac{b_a b_c}{b_a + b_c} \right) \left(\frac{\Delta E}{\Delta i} \right)^{-1}$$

where i_{corr} = corrosion current density which is a measure of corrosion rate

b_a and b_c = anodic and cathodic Tafel slope, respectively

$\frac{\Delta E}{\Delta i}$ = change of electrode potential with current density

The value of the corrosion current density can be determined using a Tafel extrapolation technique or a linear polarization procedure. Once the corrosion current is known, it can be converted to the corrosion rate by using the relationship (16)

$$\text{corrosion rate} = \frac{0.13 (i_{\text{corr}})(\text{eq.wt.})}{p}$$

where eq. wt. = equivalent weight of the metal (g)

p = metal density (gcm⁻³)

i_{corr} = current density (amp cm⁻²)

The corrosion rate also can be measured by determining the weight loss of a corroding metal after a certain time. The rate is calculated by using the general equation (17)

$$r = \frac{Kw}{pAt}$$

where r = corrosion rate

K = constant (equal to 3.45 x 10⁶ if
r is reported in mils/yr or mpy)

w = weight loss to the nearest mg
(corrected for any loss during cleaning)

t = time in hours

p = metal density (g cm⁻³)

A = surface area of the metal (cm²).

SECTION 5

EXPERIMENTAL METHODS AND MATERIALS

Evaluation of the CaCO_3 Saturation State

Different synthetic waters were prepared by mixing various proportions of stock solutions of CaCl_2 , MgSO_4 , NaHCO_3 , NaOH , HCl , or H_2SO_4 . The pH, Ca level, and alkalinity were adjusted to have waters with saturation indices ranging from -2.0 to +2.0. The actual saturation state with respect to CaCO_3 was determined for each water by adding 0.25-0.3 g of analytical reagent CaCO_3 powder to a 250-ml Erlenmeyer flask which was completely filled with the test water. The covered flask with a stirring bar was then equilibrated and shaken gently in a water bath maintained at $25 \pm 1^\circ\text{C}$. Before and after equilibration for 24 hours, the pH, Ca, and alkalinity of the test water was determined using the methods described in the section for chemical analysis. The difference between the initial and final Ca concentrations before and after equilibration was used as the basis for deciding whether the water was saturated with CaCO_3 (18).

Laboratory Studies on Corrosion

Two sets of corrosion evaluations were conducted. One utilized a static system (non-flowing) in which several jars containing water were used. The other was a loop system in which a water reservoir was connected to PVC pipes with sample specimens having different inside diameters.

Jar Tests

All the waters evaluated for the CaCO_3 saturation state were studied in jar tests. Each jar had eight small holes and a large hole in the center of the top cover as shown in Figure 3. Instrumental probes could be inserted through either the small or large hole at the appropriate time intervals for taking readings of dissolved oxygen, pH, temperature, and conductivity. Each jar with the test water and a stirring bar was positioned on top of a stirring device that provided gentle agitation of 30 rpm as shown in Figure 4. Three metal coupons were used in each test at the specified exposure period. Only one surface of each coupon was polished, while the other surface and remaining edges were coated with Microshield (a product of Michigan Chrome and Chemical Co.) to protect corrosion on these surfaces. The coupon had been previously treated by cleaning the polished surface with an abrasive powder and then rinsing with deionized water and acetone. A control coupon completely coated with Microshield was used in each jar. The oven-dried weight of the coupon

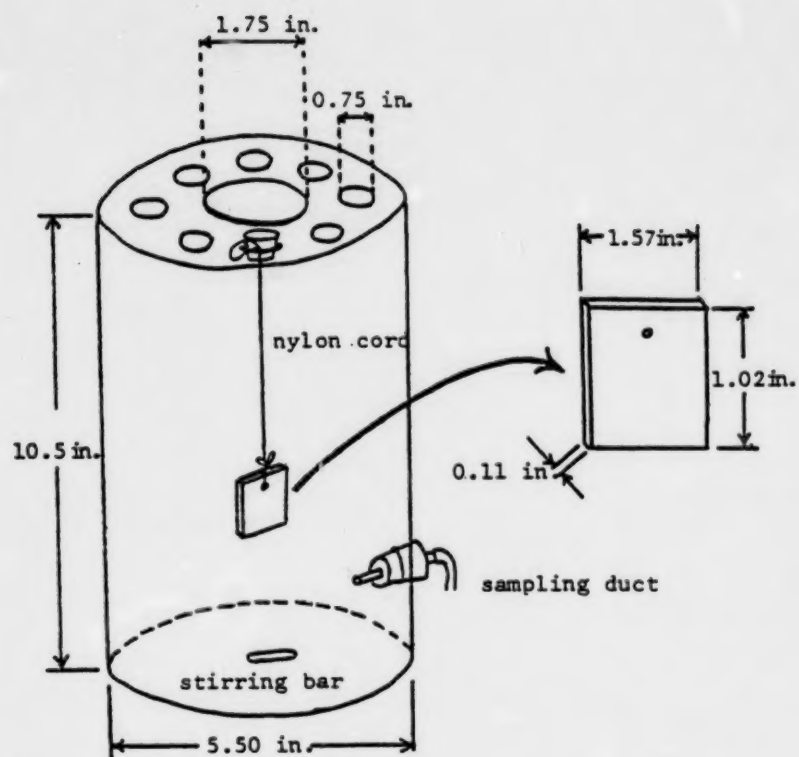


Figure 3. Diagram of a Jar Set-up and a Metal Coupon.

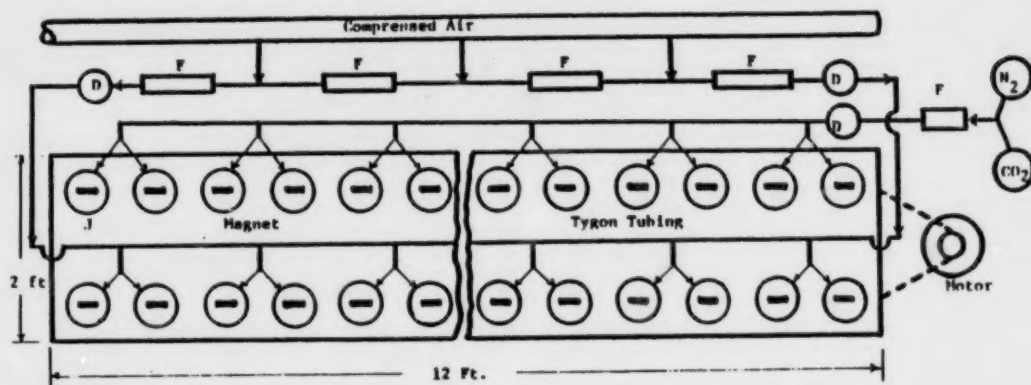


Figure 4. Stirring Apparatus. D = Deionized Water; F = Glass Wool Filter; J = Testing Jars.

before and after immersion in the test water was recorded. The loss of weight, measured to the nearest mg, was determined and used in the calculation of the corrosion rate according to the formula

$$(\text{mpy}) = \frac{534m}{pAt}$$

where m = loss of weight (mg),
p = metal density (g cm⁻³),
A = area of the exposed metal surface (in²), and
t = exposure time (hours).

In the initial phase of the studies, the coupons for the mild steel and copper specimens were embedded in epoxy except for one face that was exposed to the solution. An acrylic rod was mounted in the epoxy on the back of the coupon for the purpose of suspending the coupon in the test solution. The dimensions of the coupons were: Mild steel, 45 x 15 x 3.2mm, and copper, 30 x 15 x 1.6mm. The galvanized steel coupons, which were not embedded in the epoxy, had the dimensions 30 x 22 x 3.2mm. In addition to the weight-loss method, the corrosion rate was electronically monitored at specific time intervals using a Magna Corratel Model 1120 which employed three-electrode probes. All the corrosion experiments in the jar systems were conducted at room temperature (20±3°C). During each time interval, the change in water quality parameters, especially those that relate to pH_s or SI, were evaluated.

In jar experiments involving the effects of pH, Alk, and B (buffer capacity) on corrosion, CO₂ and air were used in adjusting the pH to the desired value as patterned upon the procedure of Roberts and Allen (19). With the rest of the jar tests, HCl or NaOH was used as needed for pH adjustment.

Loop Studies

A loop system, as schematically illustrated in Figure 5, was constructed to study corrosion of metals in contact with circulating waters of different saturation indices. All the construction materials used were non-metallic in order to prevent pick-up or leaching of metal ions. The set-up has been designed to be able to hold metal pipe specimens with different diameters (1-, 3/4-, and 1/2-inches). A Manostat Varistaltic pump (advanced model) was connected to the water reservoir to feed the pipe sections and thus regulate the water flow. This device was able to control the water velocity. Bypass tubes were provided to prevent disrupting the entire system operation when removing metal specimens for examination and analysis. Four metal pipe specimens with Microshield-coated external surfaces and edges were inserted through a PVC pipe section for corrosion evaluation. The metal inserts were aligned by using two PVC spacers on each end of the PVC sample holder. Figure 6 diagrammatically illustrates the design of the PVC pipe section that held the

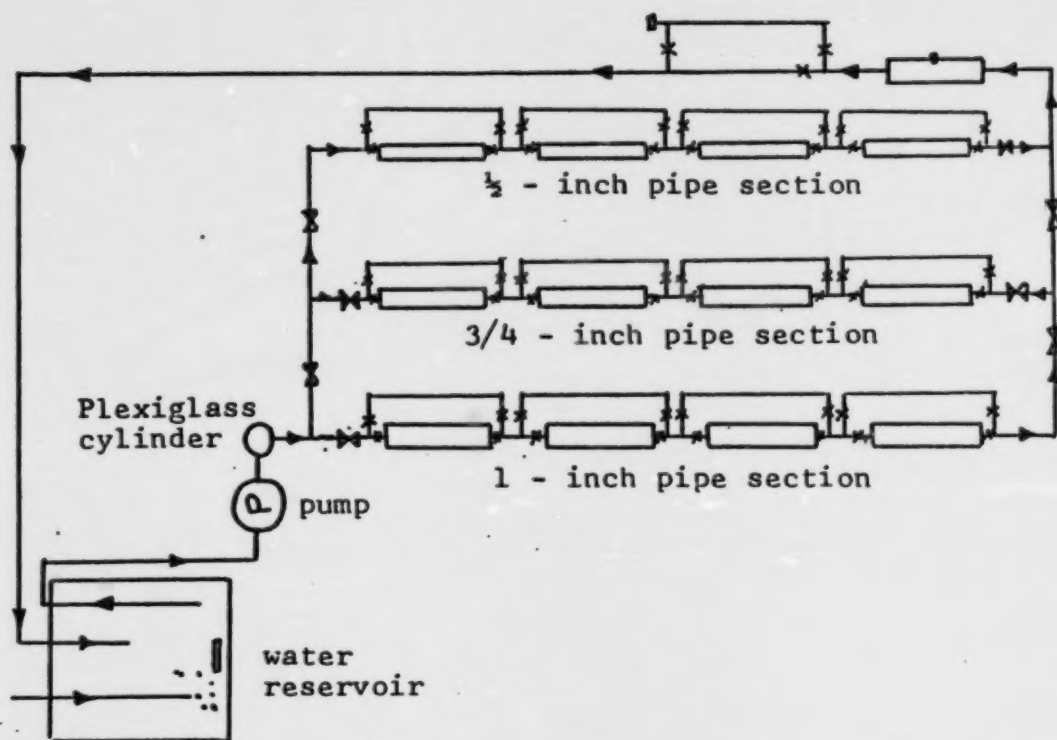


Figure 5. Set-up of the Loop System for Corrosion Evaluation of Circulating Waters.

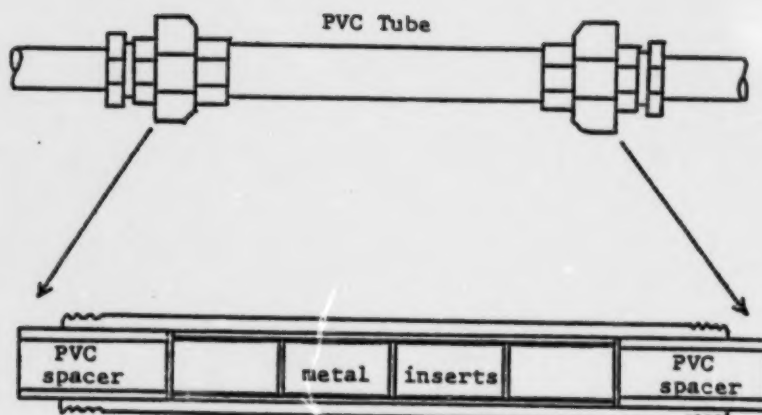


Figure 6. A PVC Tube Section of the Loop System.

metal pipe coupons. Each PVC tube section in the loop system could be disconnected and disassembled to remove the metal specimens for corrosion rate measurements.

After each corrosion test, the loop system was flushed with acidified water to remove any adhering corrosion products. This was followed by flushing with deionized water from the reservoir to rinse the entire set-up. After rinsing for several minutes an aliquot of the wash water was analyzed for the presence of metal ions in order to ensure that no metallic substances still remained in the system. As in the jar tests, the corrosion was evaluated using the weight-loss method.

Field Investigations

Field evaluation of the corrosive behavior of potable waters at two test sites was arranged with the personnel of Florida Water Utilities and South Dade Utilities. The corrosion rate and pitting index at Florida Water Utilities were monitored at various time intervals during a study period of almost 12 months. Measurement of the corrosion rate and pitting index was done at South Dade Utilities for about 10 months. Four locations were selected at Florida Water Utilities and three at South Dade Utilities systems. Corrosion was electrochemically monitored at all locations using the Magna Corrat, which measures corrosion as it occurs, not after the fact. This instrument also gives a valuable clue to the water tendency to produce pitting, which occurs where there is an uneven distribution of anode and cathode areas. Three electrode probes were installed at the study site since the resistivity of the water was high. The composition of the water was analyzed and all important water quality parameters, including CaCO_3 saturation index, were determined at appropriate sampling points in the study areas.

Chemical Analyses

The analytical procedures used in the determination of water quality parameters and other metallic ions were based on Standard Methods for the Examination of Water and Wastewater (20).

Metallic Ions: Ca, Mg, Na, Zn and Cu.

The determination of the concentration of Ca^{+2} , Mg^{+2} , Na^{+} , Zn^{+2} , and Cu^{+2} were done using an Atomic Absorption spectrophotometer. The sample preparation for each cation analysis was done with minor modification according to Standard Methods (20). The Orion Ionalyzer 901 was used in determining the activity of Ca^{+2} via a Ca^{+2} -selective electrode.

Total Dissolved Iron

Originally the concentration of dissolved iron was measured using Atomic Absorption Spectrophotometer but later according to the standardized general method for the determination of iron with 1,10 phenanthroline (21). The concentration of the standard solutions was adjusted to the range of iron concentrations normally encountered in drinking water systems. The

absorbance values of the blank and the colored samples were measured at 510 nm using a Perkin Elmer 552 spectrophotometer.

Chloride and Sulfate

Analyses of Cl^- and SO_4^{2-} were run by automated methods using the Technicon Autoanalyzer. The automated colorimetric procedures were based on the ferricyanide method for Cl^- ($\lambda = 480 \text{ nm}$) and methylthymol blue method for SO_4^{2-} ($\lambda = 460 \text{ nm}$).

pH and Alkalinity

The pH of the water samples was measured using either a research-type Corning pH meter or a Fisher Acumet Model 230A pH/ion meter after calibrating the instrument with two standard solutions whose pH values bracket the expected range of readings. The alkalinity was determined by titrating the water sample with a standardized 0.02 N H_2SO_4 in a flask covered with a rubber stopper with a hole through which the buret tip was inserted. This is similar to the method of Shock et al. (22). Bromcresol Green-Methyl Red solution, and occasionally phenolphthalein, was used as the color indicator during the acid titration to about pH 4.3.

Dissolved Oxygen and Conductivity

Both DO and conductivity of the water samples were measured instrumentally. The amount of dissolved oxygen was determined using a YSI Model 51A oxygen meter which had been previously calibrated to the oxygen concentration at the temperature of the water samples. A YSI Model 31 conductivity bridge was used in determining the solution conductivity.

Chlorine Residual Determination

Chlorine residuals were measured by amperometric titration or by the DPD (N, N -diethyl -p-phenylenediamine) method depending on the sample size. The use of the amperometric technique was preferred over the DPD method when ample volume of the sample was available.

Color Measurements

The natural color used in the experiments was obtained from Lake Weir, located near Ocala, Florida. About 50 gallons of lake water was freeze-concentrated to a final volume of 5 gallons. The final color of the concentrate, as measured by a spectrophotometer at $\lambda = 420 \text{ nm}$, was 3800 color units based on the platinum cobalt scale. All color measurements for standards and samples were made at an adjusted pH of 7.6.

Eh Measurements.

All redox potential or Eh determinations were made using an Orion Research Model 701 A digital pH/mv meter. A platinum combination electrode in conjunction with a saturated calomel reference electrode was used.

X-Ray Diffraction

Corrosion products obtained from loop studies were dried in the oven for one hour and were analyzed by X-Ray diffraction. X-Ray diffractograms of standard compounds were run simultaneously during the sample analysis.

SECTION 6

CALCIUM CARBONATE SATURATION CONCEPTS AND CORROSIVITY INDICES

The use of CaCO_3 precipitation for water pipe protection dates back to the early 1900s. Tilmans (23) in 1912 was the first to propose the CaCO_3 protection theory for corrosion control. Later in 1936, Langelier (8) derived a formula for determining the theoretical pH of CaCO_3 saturation by applying thermodynamic analysis of the CaCO_3 solubility equilibrium. He called the pH of CaCO_3 saturation " pH_s " determined by

$$\text{pH}_s = -\log \left\{ \frac{K_2}{K_s} [\text{Ca}^{+2}] [\text{Alk}] \right\}$$

or

$$\text{pH}_s = \text{p}K_2 - \text{p}K_s + \text{p}[\text{Ca}] + \text{p}[\text{Alk}]$$

where K_s = solubility product constant of CaCO_3 ;

K_2 = second dissociation constant of H_2CO_3 ; and

$[\text{Ca}^{+2}]$ and $[\text{Alk}]$ = calcium concentration and alkalinity in moles/liter and equivalents/liter, respectively.

The notation $\text{p}X = -\log X$ has been used in the second formula. Langelier proposed that the CaCO_3 saturation index of a given water could be determined using

$$\text{SI} = \text{pH}_a - \text{pH}_s$$

where SI = Saturation Index or Langelier Index,

pH_a = actual pH of the water, and

pH_s = pH at which the water is in equilibrium with CaCO_3 .

The significance of the values of SI are explained in Table 3.

In the same year the Langelier Index was introduced to the water works industry, a German investigator, Strohecker (24) developed another formula for determining the pH of CaCO_3 equilibrium

$$\text{pH}_{\text{equil}} = 11.49 - \log (\text{bound CO}_2) - \log \text{CaO}$$

Table 3. Indices of Corrosivity and Interpretation of Their Scale Values

Index Name	Reference
(1) <u>Langelier Index (1936)</u>	8
$SI = pH_a - pH_s$: pH_a and pH_s refer to actual pH and calculated pH of $CaCO_3$ saturation, respectively. $SI < 0 (-)$: non-scale forming, undersaturated $SI = 0$: stable or at equilibrium, saturated $SI > 0 (+)$: scale forming, oversaturated	
(2) <u>Ryznar Index (1944)</u>	30
$RI = 2pH_s - pH_a$: pH_s and pH_a have the same meaning as in expression for SI $RI < 6$: non-corrosive $RI = 6-7$: stable $RI > 7$: corrosive	
(3) <u>Riddick Corrosion Index (1944)</u>	32
$CI = \frac{75}{ATK} \left[CO_2 - \frac{1}{2}(Hardness - Alk) + CI^- + 2NO_3^- \right] \times A \times B$ where $A = \frac{10}{SiO_2}$ and $B = \frac{DO-2}{Sat'd. DO}$ (Factors A and B are included if values for silica (SiO_2) and dissolved oxygen (DO) are known. All parameters in the equation are in mg/l.) $CI = 0-5$: extremely non-corrosive $6-25$: non-corrosive $26-50$: moderately corrosive $51-75$: corrosive $76-100$: very corrosive >100 : extremely corrosive	
(4) <u>Casil Index (1948)</u>	33
$Casil\ Index = Ca + Mg + HSiO_3 - \frac{Anions}{2}$ $Index < 0$ or $-$: very corrosive $0-10$: slightly corrosive >10.0 : non-corrosive	

and defined the saturation index as

$$SI = pH_{\text{equil}} - pH_{\text{actual}}$$

Both Langelier's formula and Strohecker's equation were derived using the same chemical principles of CaCO_3 solubility and the dissociation of carbonic acid. The principal difference, however, is that Strohecker's equation cannot be used for computing the equilibrium pH of water containing an appreciable carbonate concentration (25).

The practical application of Langelier's method was described by Hoover (26). De Martini (25) and Langelier (27) reported practical observations of field conditions of corrosion and CaCO_3 saturation which generally confirmed the theory and formula of Langelier. Nevertheless, there were some discrepancies. The saturation index was evaluated by treating the water with excess powdered CaCO_3 or washed, precipitated CaCO_3 and determining, after settling, the pH, alkalinity, and Ca concentration (25,26). A continuous stability indicator method was described by Enslow (28,29) in which water was allowed to equilibrate as it was circulated for almost 3 hours in a system in contact with marble chips.

The Langelier method for determining the CaCO_3 saturation index was slightly modified later to account for ionic strength effects. Larson and Buswell (9) introduced such a correction term and added it to Langelier's pH_s equation to yield

$$pH_s = pK_2 - pK_s + pCa + pAlk + 9.30 + \frac{2.5\sqrt{I}}{1 + 5.3\sqrt{I} + 5.5I}$$

where Ca is expressed as mg/l and Alk as mg/l as CaCO_3 . Ryznar (30) modified the SI expression based on field observations and proposed that the stability of a water be determined using his stability index, which became known as the Ryznar Index

$$RI = 2pH_s - pH_a$$

The interpretation of Ryznar Index (RI) values is presented in Table 3. Both the Langelier Index and the Ryznar Stability Index have been used as corrosivity indices or corrosion indicators despite the fact that the values obtained were strictly a measure of the tendency of a given water to deposit or dissolve CaCO_3 . Other corrosion indices which relate to a certain extent to Ca content and alkalinity have been reported. In addition to Ca and Alk, other water quality parameters were used by Riddick (31,32) in formulating his corrosion index, (CI)

$$CI = \frac{75}{Alk} [Co_2 - \frac{1}{2}(Hard - Alk) + Cl^- + 2NO_3^-]$$

Loschiavo (33) introduced another corrosion indicator which was called Casil Index and was expressed as

$$\text{Casil Index} = \text{Ca} + \text{Mg} + \text{HSiO}_3 - \frac{\text{Anions}}{2}$$

where the concentrations of the indicated water quality parameters are in equivalents/million or simply milliequivalents/liter. The meanings associated with the values of both the Riddick and Casil Indices are shown in Table 3.

In 1946, Langelier presented diagrams for quantitative interpretation of his saturation index at normal and elevated temperatures for use in lime-soda softening and water conditioning. He also described the construction of a diagram for the conversion of room temperature pH to values at other temperatures (134). When the pH of the water sample is greater than 10.0, $\text{SI} = 10.0 - \text{pH}_s$ (135).

Dye (136) showed that the water's stability toward CaCO_3 could be obtained by knowing the excess or deficiency of CO_2 . He later proposed the concept of momentary excess of CaCO_3 (37) and reviewed its application in anti-corrosion water treatment (38). The amount of CaCO_3 that potentially can precipitate can be determined using

$$K_s = ([\text{Ca}^{+2}] - X) (\text{CO}_3^{-2}) - X$$

where X refers to the amount of precipitate required to establish equilibrium. Another measure of the tendency to deposit CaCO_3 was introduced by McCauley (39). This was known as the driving force index (DFI) and was expressed as

$$\text{DFI} = \frac{(\text{Ca}^{+2}) (\text{CO}_3^{-2})}{(K_s \times 10^{10})}$$

where Ca^{+2} and CO_3^{-2} are in mg/L as CaCO_3 . McCauley and his co-workers, as well as other investigators (40-45), applied this concept to deposit CaCO_3 coatings for pipe protection in the presence and absence of phosphates.

An instrument known as carbonate saturometer was described by Weyl (46) which can measure the degree of departure of most aqueous solutions from saturation with respect to solid carbonates. However, the instrument can be absolutely calibrated only for waters of geologic origin.

Another concept related to pH_s was recently introduced. This was the

critical pH (pH_c) which was defined by Feitler (47) as the pH above the equilibrium pH_s at which CaCO_3 actually precipitates. He devised a method to monitor the scaling tendencies of cooling water systems (48) and later proposed critical pH scaling indexes (49). There were some unexplained deviations in actual practice which Feitler could not explain, thus, his concept was viewed with doubt.

An expression for pHs was recently derived and proposed by Singley and Thompson (50) that utilized equilibrium speciation and analytical concepts of CaCO_3 chemistry. However, a fundamental error was found in the derivation.

In the last few years, there has been a resurgence of interest in utilizing CaCO_3 saturation theory. The water conditioning diagrams, as originally developed by Caldwell and Lawrence (51), were modified by Lowenthal and Marais (52) and were popularized by Merrill and Sanks (18,53,54) for use in corrosion control by deposition of a CaCO_3 film. Lately, McClelland and Mancy (55,56) described an instrument that could evaluate the actual CaCO_3 deposition potential of waters. The authors claimed that this Calcium Carbonate Deposition Test (CCDT) is much better than using Ryznar Stability Index (56).

SECTION 7

DEVELOPMENT OF ALTERNATIVE CALCULATION METHODS FOR pH_s .

The current method of evaluating the corrosive tendency of a given water is to use the Langelier or Ryznar Index:

$$\text{Langelier Index} = pH_a - pH_s$$

$$\text{Ryznar Index} = 2pH_s - pH_a$$

where pH_a = actual or measured pH of the water

pH_s = calculated pH of $CaCO_3$ saturation

In both cases, accurate determination of pH_s is critical since pH can be measured directly with a pH meter.

Because all the previously reported methods of calculating pH_s have certain limitations and are not accurate enough for many uses, there is a distinct need to explore alternative ways of accurately determining pH_s . All of the chemical events related to calcium carbonate precipitation or dissolution have to be considered in developing a better and more accurate pH_s equation. Hence, all possible equilibrium reactions affecting the concentration of Ca^{+2} and CO_3^{-2} ions were taken into account in constructing a rigorous model of $CaCO_3$ saturation.

A Chemical Model of $CaCO_3$ Solubility

Figure 7 shows various reactions affecting the solubility equilibrium of $CaCO_3$ which is indicated by bold lines in the diagram. The quantities of free Ca^{+2} and CO_3^{-2} ions are regulated by many other equilibria, including the extent of formation of ion pairs. All of these equilibria are also related to the hydrolysis of water and sequential dissociation of carbonic acid. If the formation of ion pairs such as $CaHCO_3^+$, $CaSO_4^0$, and $CaOH^+$ is significant, the concentration of free Ca^{+2} ions would be reduced, thereby decreasing the thermodynamic potential of $CaCO_3$ precipitation. Thus, the reverse process or dissolution would be favored. The same line of reasoning applies to the reduction of free CO_3^{-2} ions. Extensive ion pairing may occur between this anion and various cations, especially Mg^{+2} , present in the aqueous medium. In addition, any decrease in pH would shift the equilibrium of the second ionization of carbonic acid in favor of bicarbonate formation.

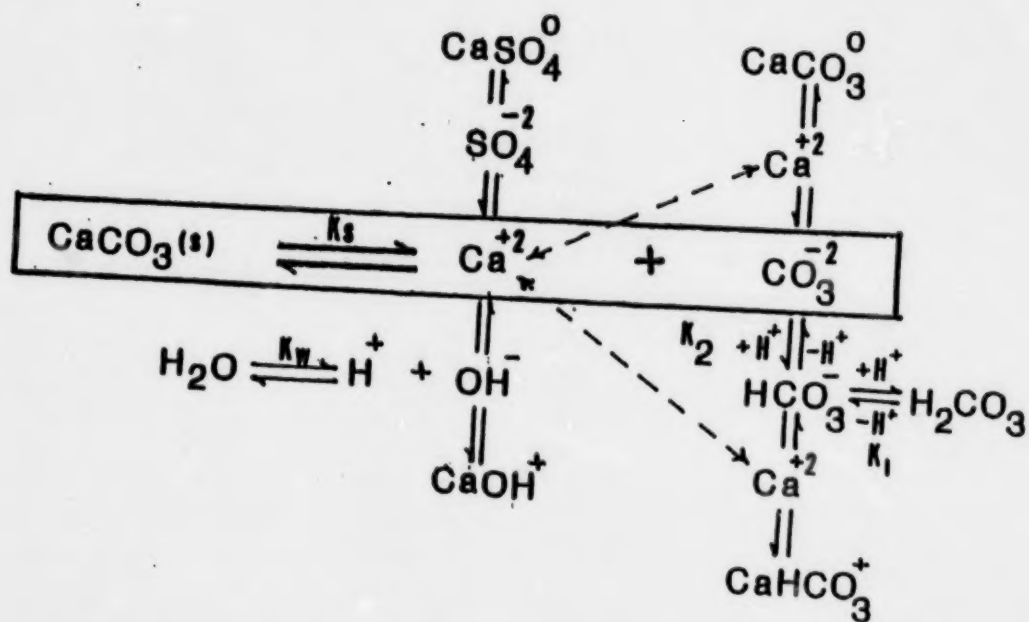


Figure 7. Chemical Model Showing Fundamental Equilibrium Relationships in Calcium Carbonate Saturation.

The ionic interaction of other cations with anions present in appreciable quantities affects the overall chemistry of CaCO_3 solubility. Such interactions could produce loosely bound charged or uncharged species or ion pairs which have been reported to be present in natural waters (5, 58) as well as in waters in the treatment plants (59, 60). Figure 8

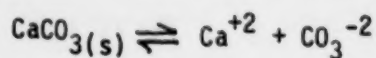
shows additional ion pairs resulting from the ionic association of Mg^{+2} and Na^{+1} with HCO_3^- , SO_4^{-2} , CO_3^{-2} , and OH^- ions. In hard waters with high levels of Mg^{+2} and SO_4^{-2} , considerable formation of MgSO_4° and MgHCO_3° have been noted. This could affect the ionic composition as well as the ionic strength of the water, and therefore, influence the driving force for CaCO_3 precipitation. Whether all or only some of the ion pairs depicted in Figures 7 or 8 would significantly interfere with CaCO_3 deposition still remains an unanswered question.

Derivation of Two New pH_s Equations

Two new and improved pH_s equations were developed. Both equations were derived by utilizing the CaCO_3 solubility equilibrium, sequential ionization of carbonic acid, and hydrolysis of water in addition to the analytical parameters often used in basic carbonate chemistry. The first equation developed was a quadratic pH_s formula utilizing a chemical model of CaCO_3 which included all the ion pairs presented in Figures 7 and 8. The second one was derived without taking into account ion pair formation.

Quadratic pH_s Formula

Using the solubility equilibrium reaction



an ion activity product for CaCO_3 (K_s) can be expressed as

$$K_s = [\text{Ca}^{+2}]_e \gamma_{\text{Ca}^{+2}} [\text{CO}_3^{-2}]_e \gamma_{\text{CO}_3^{-2}} \quad (4)$$

where $[\text{Ca}^{+2}]_e$ and $[\text{CO}_3^{-2}]_e$ = equilibrium molar concentration of calcium and carbonate ions, respectively.

$\gamma_{\text{Ca}^{+2}}$ and $\gamma_{\text{CO}_3^{-2}}$ = activity coefficient of calcium and carbonate ions, respectively.

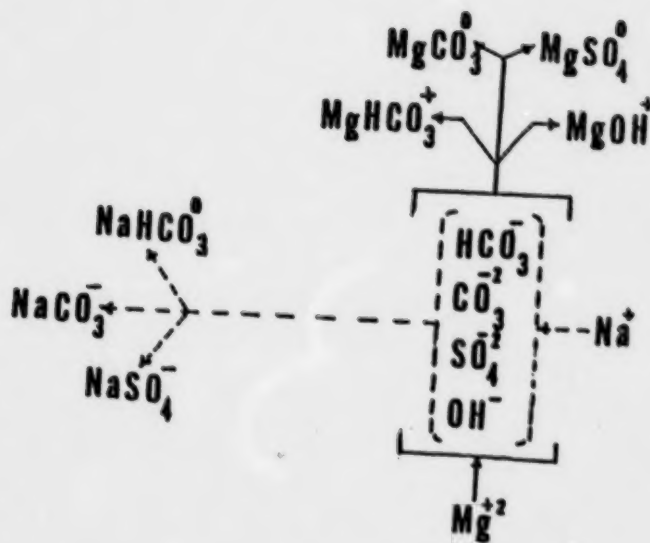


Figure 8. Ionic Association of Mg^{+2} and Na^{+} with Important Anions Commonly Occurring in Potable Water Systems.

The subscript e denotes equilibrium conditions. The fraction of the total carbonate species existing as CO_3^{-2} (α_2) is

$$\alpha_2 = \frac{[\text{CO}_3^{-2}]_T}{C_T}$$

where C_T = total carbonate species concentration

$$= [\text{H}_2\text{CO}_3^*]_T + [\text{HCO}_3^-]_T + [\text{CO}_3^{-2}]_T.$$

The subscript T indicates total molar concentration of the indicated species. Under equilibrium conditions, a similar expression for α_2 can be used, that is,

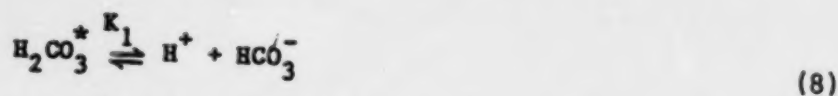
$$\alpha_2' = \frac{[\text{CO}_3^{-2}]_e}{C_T} \quad (5)$$

where $C_T' = [\text{H}_2\text{CO}_3^*]_e + [\text{HCO}_3^-]_e + [\text{CO}_3^{-2}]_e \quad (6)$

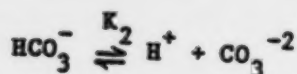
Therefore,

$$\alpha_2' = \frac{1}{\frac{[\text{H}_2\text{CO}_3^*]_e}{[\text{CO}_3^{-2}]_e} + \frac{[\text{HCO}_3^-]_e}{[\text{CO}_3^{-2}]_e} + 1} \quad (7)$$

The ratios of the indicated carbonates species in the denominator of equation (7) can be evaluated from the first and second dissociation constants of carbonic acid (K_1 and K_2) as follows



$$K_1 = \frac{\{\text{H}^+\} [\text{HCO}_3^-]_e \gamma_{\text{HCO}_3^-}}{[\text{H}_2\text{CO}_3^*] \gamma_{\text{H}_2\text{CO}_3}}$$



$$K_2 = \frac{\{\text{H}^+\} [\text{CO}_3^{-2}]_e \gamma_{\text{CO}_3^{-2}}}{[\text{HCO}_3^-]_e \gamma_{\text{HCO}_3^-}} \quad (9)$$

where the value of (i) , $[i]_e$, and γ_i respectively indicates activity, equilibrium molar concentration, and activity coefficient of species i .

From equation (8)

$$[\text{H}_2\text{CO}_3^*]_e = \frac{\{\text{H}^+\} [\text{HCO}_3^-]_e \gamma_{\text{HCO}_3^-}}{K_1} \quad (10)$$

where the value of H_2CO_3 has been assumed equal to unity since H_2CO_3 is a neutral specie.

From equation (9),

$$[\text{CO}_3^{-2}]_e = \frac{K_2 [\text{HCO}_3^-]_e \gamma_{\text{HCO}_3^-}}{\{\text{H}^+\} \gamma_{\text{CO}_3^{-2}}} \quad (11)$$

and,

$$\frac{[\text{HCO}_3^-]_e}{[\text{CO}_3^{-2}]_e} = \frac{\{\text{H}^+\} \gamma_{\text{CO}_3^{-2}}}{K_2 \gamma_{\text{HCO}_3^-}} \quad (12)$$

Dividing equation (11) by equation (10),

$$\frac{[\text{H}_2\text{CO}_3^*]_e}{[\text{CO}_3^{-2}]_e} = \frac{\{\text{H}^+\}^2 \gamma_{\text{CO}_3^{-2}}}{K_1 K_2} \quad (13)$$

Substituting equation (12) and equation (13) into equation (7),

$$\alpha_2' = \frac{1}{\frac{\{\text{H}^+\}^2 \gamma_{\text{CO}_3^{-2}}}{K_1 K_2} + \frac{\{\text{H}^+\} \gamma_{\text{CO}_3^{-2}}}{K_2 \gamma_{\text{HCO}_3^-}} + 1} \quad (14)$$

Multiplying equation (14) by $K_1 K_2 / K_1 K_2$,

$$\alpha_2' = \frac{K_1 K_2}{\{\text{H}^+\}^2 \gamma_{\text{CO}_3^{-2}} + \frac{K_1 \{\text{H}^+\} \gamma_{\text{CO}_3^{-2}}}{\gamma_{\text{HCO}_3^-}} + K_1 K_2} \quad (15)$$

Using equation (5) in equation (4) and rearranging,

$$\alpha_2' = \frac{K_s}{[Ca^{+2}]_e \gamma_{Ca^{+2}} \gamma_{CO_3^{-2}} C_T} \quad (16)$$

Comparing equations (15) and (16),

$$\frac{K_1 K_2}{\{H^+\}^2 CO_3^{-2} + \frac{K_1 \{H^+\} \gamma_{CO_3^{-2}}}{\gamma_{HCO_3^-}} + K_1 K_2} = \frac{K_s}{[Ca^{+2}]_e \gamma_{Ca^{+2}} \gamma_{CO_3^{-2}} C_T}$$

which can be rewritten at $CaCO_3$ saturation as

$$\left\{H_s^+\right\}^2 \gamma_{CO_3^{-2}} + \left\{H_s^+\right\} \frac{K_2 \gamma_{CO_3^{-2}}}{\gamma_{HCO_3^-}} + K_1 K_2 - \frac{K_1 K_2 [Ca^{+2}]_e \gamma_{Ca^{+2}} \gamma_{CO_3^{-2}} C_T'}{K_s} = 0 \quad (17)$$

The value of $\{H_s^+\}$ can be obtained by applying the quadratic formula

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$$

to equation (17) in which

$$x = \{H_s^+\},$$

$$a = \gamma_{CO_3^{-2}},$$

$$b = K_1 \frac{\gamma_{CO_3^{-2}}}{\gamma_{HCO_3^-}}, \text{ and}$$

$$c = K_1 K_2 - \frac{K_1 K_2 [Ca^{+2}]_e \gamma_{Ca^{+2}} \gamma_{CO_3^{-2}} c_T'}{K_s}$$

Therefore, the final form of the equation for hydrogen activity at $CaCO_3$ saturation becomes

$$\{H_s^+\} = \left[\frac{K_1^2}{4 \gamma_{HCO_3^-}} - \frac{K_1 K_2}{\gamma_{CO_3^{-2}}} \left(1 - \frac{[Ca^{+2}]_e \gamma_{Ca^{+2}} \gamma_{CO_3^{-2}} c_T'}{K_s} \right) \right]^{1/2} \quad (18)$$

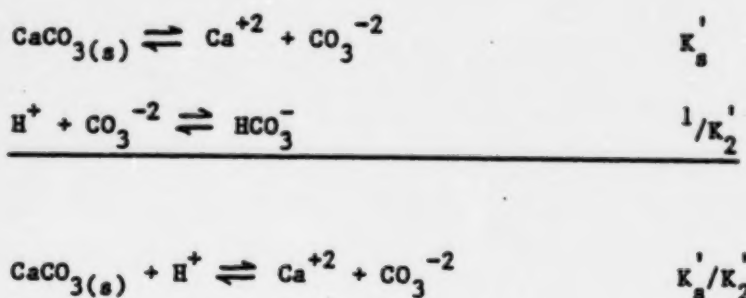
$$- \frac{K_1}{2 \gamma_{HCO_3^-}}$$

The value of $\{H_s^+\}$ can be solved from equation (18) by iterative calculation whereby values of the variables, except equilibrium constants at a given temperature, on the right hand side of the equation initially are given approximate values until both sides of the equation are almost numerically

equal. It must be pointed out that the equilibrium calculation would entail consideration of all ion pairs depicted in Figures 7 and 8 so as to make the evaluation of ionic strength, and in turn, activity coefficients, more accurate.

Alternative Simplified pH_s Expression.

To check whether ion pairing would exert a significant effect on the pH of CaCO₃ saturation, another formula was derived in which ion pair concentrations were neglected. This time the approach was based on the effect of H⁺ on the solubility of CaCO₃ which can be developed from the following equilibria:



where K_{s1} = concentration solubility product constant of calcium carbamate.
 K_2 = second concentration dissociation constant of carbomic acid.

At CaCO₃ saturation,

$$[\text{H}_s^+] = \frac{K_2'}{K_s'} [\text{Ca}^{+2}] [\text{HCO}_3^-]$$

which could be transformed to

$$p[\text{H}_s^+] = pK_2' - pK_s' - \log \text{Ca}^{+2} - \log \text{Alk} \quad (19)$$

in the pH range 6.5 to 9.0 where $[\text{HCO}_3^-] \simeq \text{Alk}$.

To be able to use directly the thermodynamic constants K_2 and K_s , the ionic strength and activity coefficients of the ions of interest must be evaluated. In terms of the thermodynamic constants and activity coefficients, pK_2' and pK_s can be expressed as

$$pK_2' = pK_2 + \log \gamma_{H^+} + \log \gamma_{CO_3^{2-}} - \log \gamma_{HCO_3^-} \quad (20)$$

$$pK_s = pK_s + \log \gamma_{Ca^{2+}} + \log \gamma_{CO_3^{2-}} \quad (21)$$

For the hydrogen ion concentration,

$$p[H^+] = pH + \log \gamma_{H^+} \quad (22)$$

Since the ionic strengths of most drinking waters generally do not exceed 0.1 M, the extended Debye-Huckel equation can be used in evaluating the activity coefficients in equations (20), (21), and (22).

$$-\log \gamma_i = \frac{A Z_i^2 \sqrt{I}}{1 + B a \sqrt{I}} \quad (23)$$

The values of constants A and B at 25°C are 0.50 and 0.33, respectively, while the adjustable parameter for each ion is available from the work of Kielland (145). Using these values and applying (23), the following expressions for activity coefficients result:

$$\log \gamma_{H^+} = - \frac{0.5 \sqrt{I}}{1 + (0.33) (9) \sqrt{I}}$$

$$\log \gamma_{Ca^{2+}} = - \frac{0.5 (4) \sqrt{I}}{1 + (0.33) (6) \sqrt{I}}$$

$$\log \gamma_{CO_3^{2-}} = - \frac{0.5 (4) \sqrt{I}}{1 + (0.33) (5) \sqrt{I}}$$

$$\log \gamma_{HCO_3^-} = - \frac{0.5 \sqrt{I}}{1 + (0.33) (4) \sqrt{I}}$$

which can be substituted into equations (20), (21), and (22) to yield

$$pK_2' = pK_2 - \frac{0.5 \sqrt{I}}{1 + 2.97 \sqrt{I}} - \frac{2 \sqrt{I}}{1 + 1.65 \sqrt{I}} + \frac{0.5 \sqrt{I}}{1 + 1.32 \sqrt{I}} \quad (24)$$

$$pK_s' = pK_s - \frac{2 \sqrt{I}}{1 + 1.98 \sqrt{I}} - \frac{2 \sqrt{I}}{1 + 1.00 \sqrt{I}} \quad (25)$$

$$p[H^+] = pH - \frac{0.5 \sqrt{I}}{1 + 2.97 \sqrt{I}} \quad (26)$$

Substituting equations (24) to (26) in equation (19) gives another expression of pH_s

$$pH_s = pK_2 - pK_s - \log [Ca^{+2}]_T - \log Alk + \frac{2.5 \sqrt{I} + 3.63 I}{1 + 3.30 \sqrt{I} + 2.61 I} \quad (27)$$

where I is the ionic strength as determined from the given ionic composition of the water. Since no ionic pairs are considered, the equilibrium Ca^{+2} concentration is assumed to be equal to the total calcium,

$[Ca^{+2}]_T$. The parameter Alk or alkalinity in equation (27) is expressed in equivalents/liter. For comparison, Table 4 presents the pH_s equations developed by other workers and those derived from this study.

Computational Procedure for Determining pH_s

To be able to evaluate pH_s from the quadratic formula [see equation (18)], the equilibrium concentrations of the free ions and ion pairs would have to be determined. This would require several mass balance equations which have to be simultaneously solved. Generally, the concentration of the free ions are calculated by subtracting the combined concentration of ion pairs from the total concentration of the cation or anion of interest. Thus, the mass-balance expressions for the following free ions are:

$$[Ca^{+2}] = [Ca^{+2}]_T - [CaHCO_3^+] - [MgSO_4^0] - [CaCO_3^0] - [CaOH^+]$$

$$[Mg^{+2}] = [Mg^{+2}]_T - [MgHCO_3^+] - [MgSO_4^0] - [MgCO_3^0] - [MgOH^+]$$

$$[Na^{+1}] = [Na^{+1}]_T - [NaHCO_3^0] - [NaSO_4^-] - [NaCO_3^-]$$

$$[HCO_3^-] = [HCO_3^-]_T - [CaHCO_3^+] - [MgHCO_3^+] - [NaHCO_3^0]$$

$$[CO_3^{-2}] = [CO_3^{-2}]_T - [CaCO_3^0] - [MgCO_3^0] = [NaCO_3^-]$$

$$[SO_4^{-2}] = [SO_4^{-2}]_T - [CaSO_4^0] - [MgCO_4^0] = [NaSO_4^{-1}]$$

The concentrations of the ion pairs can be expressed in terms of the relevant equilibrium constants and free ion concentration as follows:

$$[\text{CaHCO}_3^+] = \frac{[\text{Ca}^{+2}] [\text{HCO}_3^-] \gamma_{\text{Ca}^{+2}} \gamma_{\text{HCO}_3^-}}{K_{\text{CaHCO}_3^+} \gamma_{\text{CaHCO}_3^+}}$$

$$[\text{CaCO}_3^0] = \frac{[\text{Ca}^{+2}] [\text{CO}_3^{-2}] \gamma_{\text{Ca}^{+2}} \gamma_{\text{CO}_3^{-2}}}{K_{\text{CaCO}_3^0}}$$

$$[\text{CaSO}_4^0] = \frac{[\text{Ca}^{+2}] [\text{SO}_4^{-2}] \gamma_{\text{Ca}^{+2}} \gamma_{\text{SO}_4^{-2}}}{K_{\text{CaSO}_4^0}}$$

$$[\text{CaOH}^+] = \frac{[\text{Ca}^{+2}] \gamma_{\text{Ca}^{+2}} K_w}{K_{\text{CaOH}^+} \gamma_{\text{CaOH}^+} \{ \text{H}^+ \}}$$

$$[\text{MgHCO}_3^+] = \frac{[\text{Mg}^{+2}] [\text{HCO}_3^-] \gamma_{\text{Mg}^{+2}} \gamma_{\text{HCO}_3^-}}{K_{\text{MgHCO}_3^+} \gamma_{\text{MgHCO}_3^+}}$$

$$[\text{MgCO}_3^0] = \frac{[\text{Mg}^{+2}] [\text{CO}_3^{-2}] \gamma_{\text{Mg}^{+2}} \gamma_{\text{CO}_3^{-2}}}{K_{\text{MgCO}_3^0}}$$

$$[\text{MgSO}_4^0] = \frac{[\text{Mg}^{+2}] [\text{SO}_4^0] \gamma_{\text{Mg}^{+2}} \gamma_{\text{SO}_4^{-2}}}{K_{\text{MgSO}_4^0}}$$

Table 4. Various Forms of Equations for Evaluating the pH of CaCO_3 Saturation

1. Langelier, 1936 (8):

$$\text{pH}_s = -\log [K_2/K_s (\text{Ca}^{+2}, \text{moles/l}) (\text{Alk}, \text{equiv/l})]$$

2. Larson-Buswell, 1942 (161):

$$\text{pH}_s = -\log [K_2/K_s (\text{Ca}^{+2}, \text{mg/l}) (\text{Alk}, \text{mg/l as CaCO}_3)] + 9.30 + \frac{2.5 \sqrt{I}}{1.0 + 5.3 \sqrt{I} + 5.5 I}$$

3. Singley-Thompson, 1977 (50):

$$\left\{ \text{H}_s^+ \right\}^2 + \left\{ \text{H}_s^+ \right\} K_1 + K_1 K_2 \left[1 - \frac{[\text{Ca}^{+2}] \gamma_{\text{Ca}^{+2}} \left\{ \text{CALC as CaCO}_3 \right\}}{(\alpha_1 + \alpha_2) K_s} \right] = 0$$

$$\text{pH}_s = -\log \left\{ \text{H}^+ \right\}$$

4. Present Studies:

(a) Simplified form (ion pair concentration neglected):

$$\text{pH}_s = -\log [K_2/K_s (\text{Ca}^{+2}, \text{moles/l}) (\text{Alk}, \text{equiv/l})] + \frac{2.5 \sqrt{I} + 3.63 I}{1.0 + 3.30 \sqrt{I} + 2.61 I}$$

(b) Quadratic form (ionic speciation considered):

$$\text{pH}_s = -\log \left\{ \left[\frac{K_1^2}{4 \gamma_{\text{HCO}_3^-}} - \frac{K_1 K_2}{\gamma_{\text{CO}_3^{2-}}} \right] \left(1 - \frac{[\text{Ca}^{+2}]_e \gamma_{\text{Ca}^{+2}} \gamma_{\text{CO}_3^{2-}}}{K_s} \right)^{1/2} - \frac{K_1}{2 \gamma_{\text{HCO}_3^-}} \right\}$$

$$[\text{MgOH}^+] = \frac{[\text{Mg}^{+2}] \gamma_{\text{Mg}^{+2}} K_w}{K_{\text{MgOH}^+} \gamma_{\text{MgOH}^+} \{ \text{H}^+ \}}$$

$$[\text{NaHCO}_3^0] = \frac{[\text{Na}^+] [\text{HCO}_3^-] \gamma_{\text{Na}^+} \gamma_{\text{HCO}_3^-}}{K_{\text{NaHCO}_3^0}}$$

$$[\text{NaCO}_3^-] = \frac{[\text{Na}^+] [\text{CO}_3^{-2}] \gamma_{\text{Na}^+} \gamma_{\text{CO}_3^{-2}}}{K_{\text{NaCO}_3^-} \gamma_{\text{NaCO}_3^-}}$$

$$[\text{NaSO}_4^-] = \frac{[\text{Na}^+] [\text{SO}_4^{-2}] \gamma_{\text{Na}^+} \gamma_{\text{SO}_4^{-2}}}{K_{\text{NaSO}_4^-} \gamma_{\text{NaSO}_4^-}}$$

Since it would be difficult to determine the equilibrium concentration of H_2CO_3^* , the evaluation of C_T^i would be a problem. Fortunately, however, C_T^i could be related to the equilibrium alkalinity which can be defined as

$$[\text{Alk}]_e = [\text{HCO}_3^-]_e + 2[\text{CO}_3^{-2}]_e$$

In terms of C_T^i ,

$$[\text{Alk}]_e = \alpha_1^i C_T^i + 2\alpha_2^i C_T^i$$

Thus,

$$C_T^i = \frac{[\text{Alk}]_e}{\alpha_1^i + 2\alpha_2^i}$$

where α_1^i and α_2^i can be solved by knowing the pH of the water and dissociation constants of carbonic acid at the specified temperature.

Because several mass-balance expressions and equilibrium equations have to be solved, a computer program for the lengthy and tedious calculation was necessary. An earlier program constructed for the evaluation of the Singley-Thompson equation has been re-examined and tested. Some modifications were done and additional subroutines were incorporated to calculate other analytical parameters pertinent to the evaluation of the accuracy of the mass-balance expressions and quality of the data on ionic composition. Figure 9 shows the flow chart of the revised computer program indicating the successive approximation procedure for determining the quadratic pH_5 , concentrations of charged and uncharged ionic species, percent free and combined ions, charge balance error, and ratio of excess charge to ionic strength. The program first reads the values of the equilibrium constants and data on the water composition. Then as a first approximation, the converted total molar concentration of each ion is used in calculating the ionic strength by calling subroutine ISA. Once an ionic strength is obtained, the values of the activity coefficients and ion pair concentrations could be determined through subroutines COEF and PAIRON. A second better estimate of ionic strength will then result. The iteration is done 3 times before the total equilibrium carbonate concentration, fractions of bicarbonate (α_1), and carbonate (α_2) of the sum of carbon species quantities are computed. By calling subroutine QUAPHS, the value of quadratic pH_5 is estimated and then compared with an initial value. If the absolute difference between the two pH_5 values is less than or equal to 0.010, the last pH_5 value is printed as the pH of $CaCO_3$ saturation of a given water. Otherwise, another iteration route is followed and successively done until the final difference is 0.010 or less. Calculation of other relevant analytical parameters follow, the values of which indicate the extent of ion pairing, excess charge, and charge balance error. Finally, the quantities of the free ions and ion pairs, determined from the iterative computation procedure, are summed up and compared with the given total concentration of each ionic species. Computer evaluation of pH_5 of another water sample is commenced by reading the composition of the next water. Aside from the introduction of three subroutines, new values of some equilibrium constants were incorporated in the revised computer program. These constants were recent values at 25°C found in the literature and are presented in Table 5. The K_5 value formerly used was that of Larson and Buswell (9). Recent studies, however, have indicated that the K_5 value derived by Larson and Buswell using the data of Frear and Johnston (61), was incompatible with experimental results (62). The pK_5 value (8.42) used in the present computer calculation is slightly lower than 8.52 reported by Christ et al. (63) and greater than 7.97 from the studies of Suarez (64) on the ion activity product of $CaCO_3$ in the soil-root system. The earlier K_1 value of 4.31×10^{-7} (65) is closer to 4.32×10^{-7} (66) which was used in this study. The new value of

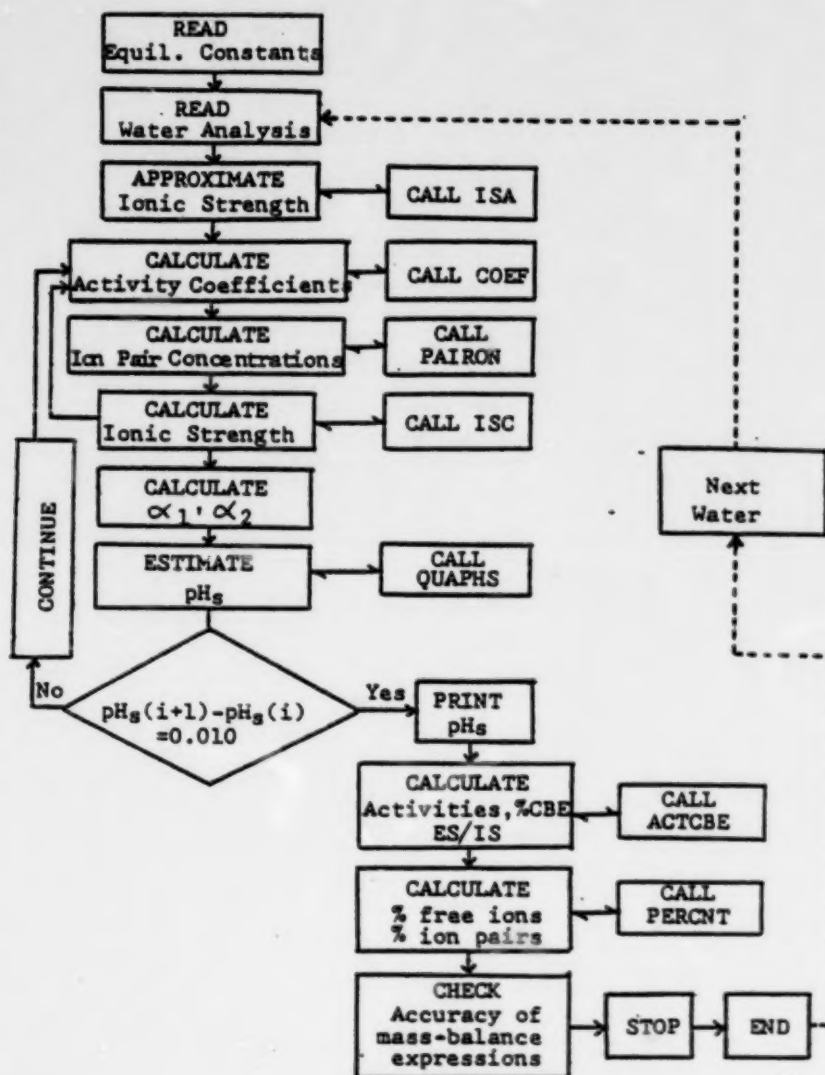


Figure 9. Flow Diagram of the Iterative Computational Steps for Calculating pHs, Concentrations of Free Ions and Ion Pairs, and Relevant Analytical Parameters. (CBE = Charge Balance Error; ES = Excess Charge; IS = Ionic Strength)

K_2 (4.786×10^{-11}) was computed using pK_2 (10.32) of Helgeson (67) and was higher than 4.69×10^{-11} , the value from Harned and Sholes (68) which was used before. The equilibrium association constants of the ion pairs were taken from the work of Larson and Sollo (69). Although the constants A and B can be expressed as functions of temperature, their values were not calculated but instead were taken from the table prepared by Midgley and Torrance (70). The two constants were used in the calculation of the activity coefficient of each ionic species according to the extended Debye-Huckel equation. The values of "a" or the ion size parameters were taken from Kielland (71). A value of 4.0 was assigned to the size parameters of the following ion pairs: CaHCO_3^+ , CaOH^+ , MgHCO_3^+ , MgOH^+ , NaSO_4^- , and NaCO_3^- .¹

¹ Personal communication with Dr. Roger Bates, Professor of Analytical Chemistry, University of Florida.

Table 5. Values of the Constants at 25°C Used in the Computer Calculation of the pH_s of the Water Samples Using the Quadratic Formula.

Constant	Value	-log Constant	Reference
K ₁	0.432 x 10 ⁻⁶	6.365	66
K ₂	4.786 x 10 ⁻¹¹	10.32	67
K _s	3.802 x 10 ⁻⁹	8.42	62
K _w	0.1010 x 10 ⁻¹³	14.00	72
K _{CaHCO₃⁺}	0.550 x 10 ⁻¹	1.26	69
K _{CaSO₄[•]}	0.490 x 10 ⁻²	2.31	69
K _{CaCO₃[•]}	0.599 x 10 ⁻³	3.22	69
K _{CaOH⁺}	0.4166 x 10 ⁻¹	1.38	69
K _{MgHCO₃⁺}	0.690 x 10 ⁻¹	1.16	69
K _{MgSO₄[•]}	0.230 x 10 ⁻²	2.64	69
K _{MgCO₃[•]}	0.126 x 10 ⁻²	2.90	69
K _{MgOH⁺}	0.830 x 10 ⁻²	2.09	69
K _{NaHCO₃[•]}	0.180 x 10 ⁻²	0.26	69
K _{NaSO₄⁻}	0.190 x 10 ⁻¹	1.72	69
K _{NaCO₃⁻}	0.540 x 10 ⁻¹	1.27	69
A*	0.512		70
B*	0.329		70

* Constants in the Debye-Huckel equation.

SECTION 8

RESULTS AND DISCUSSION

Studies on the pH of Calcium Carbonate Saturation Evaluation of the pHs of 155 Water Samples Using the Quadratic pHs Formula

The quadratic pH_s equation, which was derived by taking into account ion pairing and activity correction factors, was used in determining the pH of calcium carbonate saturation of 155 Florida water samples. The calculation was done using a revised computer program developed from the Singley-Thompson equation. The main computer program including the subroutines was stored and run in the University of Florida computer system. The chemical composition of the water samples was taken from the report of U.S. Geological Survey (73) who conducted a recent study of the chemical, physical, and radiological quality of selected public water supplies in Florida. Table 6 lists the analytical parameters obtained at $25 \pm 5^\circ\text{C}$ for the water samples used in the pH_s evaluation. A summary of the mean values and range of the analytical parameters is presented in Table 7. It should be noted that the range for each analytical variable is wide enough to cover the spectrum of water analyses commonly encountered in potable water systems. For instance, the typical TDS of 50 to 500 mg/l of most waters is within the range 44 to 1,774 mg/l. The same holds true for the major cations, Ca^{+2} , Mg^{+2} , Na^+ , as well as the important anions, SO_4^{-2} , Cl^- , and HCO_3^- . Most of the waters have sufficient hardness which is characteristic of most waters in Florida compared with waters with low hardness found in many other states.

The pH_s values of the water samples range from 6.70 to 9.97 with a mean value of 7.49. Generally, some of these values are higher than the actual pH of the waters as could be inferred from the pH range of 6.20 to 9.20. However, the mean pH of 7.45 is very close to the mean pH_s .

Extent of Ion Pair Formation

The extent of ion pairing for each water sample was similarly calculated. It was found that the concentration of all sodium ion pairs was negligible. As presented in Table 8, the average percentage of Na ion pairs was about 1.1% of the total sodium ion concentration. These ion

Table 6. Analyses of the 155 Water Samples. (All values are expressed in mg/l except alkalinity (Alk) and hardness (Hard) in mg/l as CaCO₃ and pH.)

OBS	TDS	CA	MG	HA	SO4	CL	FE	F	ALK	HARD	PHI
1	768	80	48	68	180	120	0.00	1.10	284	479	7.1
2	270	84	2	0	4	8	2.00	0.00	153	171	8.1
3	77	10	2	7	9	15	0.00	1.10	21	33	8.2
4	646	62	14	105	49	87	0.20	0.13	270	212	7.1
5	693	72	31	98	82	150	0.00	0.00	289	307	7.8
6	453	103	1	13	14	27	2.10	0.00	239	265	7.1
7	293	30	17	46	33	39	0.00	0.00	131	144	7.6
8	409	98	2	20	6	40	1.70	0.00	244	255	7.0
9	312	80	2	16	26	29	0.00	0.30	194	207	7.4
10	1689	188	44	279	10	614	9.60	1.30	429	467	7.2
11	122	45	2	3	0	7	0.00	0.10	109	120	7.2
12	431	104	10	49	49	30	1.10	0.00	318	302	7.3
13	480	42	22	69	45	73	0.00	0.70	262	245	7.7
14	253	84	0	6	0	20	0.05	0.00	198	211	7.3
15	290	85	3	13	39	22	0.00	0.10	180	214	7.6
16	497	95	10	22	39	29	0.27	0.00	247	270	7.2
17	133	30	9	5	7	3	0.00	0.30	113	111	7.7
18	314	68	5	5	6	11	0.56	0.35	179	191	8.3
19	48	22	37	69	19	160	0.20	0.75	102	192	9.2
20	262	82	2	11	27	14	0.00	0.20	187	212	7.4
21	390	71	23	9	102	14	0.20	0.00	147	272	8.2
22	377	40	17	40	67	13	0.14	0.00	148	170	7.2
23	110	36	2	3	0	3	0.00	0.10	95	98	7.5
24	393	80	13	1	0	16	0.02	0.30	232	253	8.3
25	666	140	9	27	6	126	10.50	0.00	283	405	8.5
26	416	54	13	46	50	63	0.00	0.40	131	188	7.8
27	648	95	8	22	5	24	0.70	1.20	246	258	7.3
28	163	48	3	4	9	6	0.00	0.25	123	132	7.3
29	610	10	13	140	57	19	0.28	7.00	295	78	8.1
30	124	27	11	4	6	3	0.00	0.20	113	112	7.6
31	440	57	31	28	10	90	0.00	2.70	189	269	7.4
32	317	100	10	8	9	11	0.00	0.10	177	200	7.2
33	360	61	23	58	11	60	1.64	0.00	263	249	7.7
34	80	19	4	3	3	3	0.00	0.10	71	72	7.5
35	563	124	2	25	25	28	1.60	0.00	310	320	7.2
36	510	72	40	3	170	5	0.00	0.00	161	344	7.4
37	451	100	0	18	5	24	3.20	0.00	249	255	7.2
38	395	98	3	17	27	30	0.00	0.30	233	252	7.2
39	373	100	3	22	26	36	0.00	0.30	234	262	7.2
40	379	67	10	3	10	10	3.00	0.00	221	238	7.0
41	524	95	14	65	31	120	0.00	0.30	230	294	7.2
42	571	105	9	36	2	64	0.30	0.00	290	302	7.8
43	424	62	34	54	34	89	0.00	1.00	233	253	7.4
44	1240	116	58	225	172	518	0.06	0.35	128	528	7.2
45	498	100	7	48	54	85	0.00	0.30	239	278	7.3
46	447	50	29	49	15	152	0.10	1.10	124	244	7.9
47	242	6	5	78	5	30	0.00	0.60	171	35	8.0
48	1462	81	91	307	36	776	0.00	1.60	139	576	7.6
49	360	100	5	18	32	26	0.00	0.20	249	270	7.5
50	722	79	63	39	58	150	0.01	2.00	271	456	7.4
51	324	62	24	14	110	10	0.00	0.60	144	253	7.2
52	781	113	7	93	140	30	0.20	0.10	326	311	7.2
53	940	89	44	6	190	9	0.00	0.30	210	403	7.0
54	893	80	44	29	201	69	0.00	1.20	138	260	7.2
55	374	110	4	25	4	36	0.00	0.20	289	291	7.3
56	538	73	29	37	206	17	0.00	0.45	144	301	7.3
57	352	98	4	13	65	38	0.00	0.20	178	261	7.7
58	186	26	4	19	2	20	0.00	0.00	94	81	7.0
59	906	260	7	10	370	35	0.00	0.60	269	678	7.3
60	149	20	4	14	10	9	0.30	0.00	75	64	7.6
61	219	40	18	7	19	9	0.00	0.30	154	161	7.5
62	119	18	8	1	0	9	0.01	0.12	68	77	8.1
63	206	64	4	4	7	6	0.00	0.10	171	181	7.3
64	257	16	18	33	9	18	0.22	0.58	135	99	8.1
65	92	3	5	8	8	9	0.00	0.10	44	52	7.8
66	100	30	2	8	2	10	0.03	0.00	77	83	7.6
67	467	90	3	33	25	39	0.00	0.30	230	257	7.4
68	770	77	96	36	30	360	0.21	1.00	139	567	7.9
69	307	53	8	27	25	35	0.00	0.40	129	165	7.4
70	357	19	44	7	10	14	0.10	0.00	215	228	7.8
71	293	40	13	9	6	12	0.00	0.40	151	153	7.2
72	878	15	48	200	111	255	0.01	0.45	204	225	7.6
73	210	37	13	19	25	14	0.00	0.60	121	145	7.2
74	174	17	109	403	19	99	0.00	1.65	140	491	7.8
75	167	46	8	4	4	5	0.00	0.20	146	147	7.1

Table 6. Continued

OBS	TDS	CA	MG	NA	SO4	CL	FE	F	ALK	HARD	PHI
77	193	27	7	13	4	5	0.20	0.38	112	96	7.8
78	142	120	13	100	38	200	0.00	0.30	138	333	7.8
79	181	24	13	6	10	19	0.00	0.45	99	113	8.0
80	228	51	10	14	7	12	0.00	0.20	180	144	7.2
81	172	26	4	14	10	9	0.14	0.25	89	81	8.0
82	132	27	9	14	12	6	0.00	0.18	87	104	7.3
83	222	37	5	15	11	14	0.24	0.40	114	113	8.1
84	325	94	3	17	23	25	0.00	0.20	226	247	7.3
85	217	37	8	8	1	12	0.02	0.28	125	129	7.5
86	444	94	8	47	14	82	0.00	0.20	243	267	7.4
87	215	27	15	6	7	8	0.08	0.00	130	129	7.5
88	382	90	6	38	22	57	0.00	0.30	236	249	7.3
89	227	41	1	19	1	23	0.00	0.00	110	106	8.1
90	442	100	4	33	30	73	0.00	0.20	236	274	7.4
91	346	52	16	12	19	11	0.10	0.00	188	195	7.7
92	114	23	13	2	9	11	0.00	0.10	98	110	7.8
93	330	57	14	2	26	12	0.42	0.31	176	200	7.9
94	164	24	14	8	8	3	0.00	0.20	128	117	7.7
95	325	59	11	11	23	14	0.00	0.41	172	192	7.6
96	601	100	18	84	34	160	0.00	0.30	224	323	7.3
97	914	148	19	134	0	430	0.00	0.00	150	448	7.1
98	343	99	4	22	28	32	0.20	0.25	243	263	7.2
99	1136	184	17	125	188	195	2.20	0.00	364	833	7.9
100	420	46	17	59	34	91	0.00	0.50	138	189	8.1
101	485	58	28	34	98	68	0.08	0.65	138	260	7.9
102	213	50	14	5	7	4	0.00	0.20	180	182	7.3
103	430	118	6	76	9	244	0.00	0.00	152	320	7.2
104	1250	75	55	270	110	330	0.00	1.20	174	413	7.5
105	875	92	12	171	27	281	0.30	0.50	238	279	7.5
106	312	90	2	16	39	21	0.00	0.20	203	232	7.3
107	712	120	12	181	0	320	0.10	0.00	130	349	7.4
108	81	17	2	6	25	8	0.00	0.10	94	98	7.0
109	986	164	12	177	6	470	0.48	0.00	150	489	7.0
110	64	4	1	0	0	5	0.00	0.18	11	14	6.6
111	935	140	17	146	8	460	0.34	0.00	190	420	7.0
112	346	28	16	75	38	110	0.00	0.70	125	138	7.8
113	1610	139	46	266	86	565	0.08	0.15	252	536	7.1
114	153	22	4	13	16	60	0.15	0.10	16	71	7.5
115	1198	75	92	189	15	518	0.20	0.00	253	566	8.0
116	246	45	21	16	6	13	0.00	0.40	207	196	7.2
117	1426	76	85	288	167	595	0.50	1.10	175	540	7.2
118	360	119	3	18	21	28	0.00	0.20	256	287	7.1
119	398	91	7	33	45	58	0.30	0.30	210	356	7.2
120	401	69	7	58	11	120	0.02	0.10	140	201	7.9
121	109	22	2	7	27	12	0.08	0.00	31	63	7.1
122	364	42	13	60	110	83	0.04	0.10	72	158	7.8
123	328	94	3	17	40	28	0.04	0.10	150	252	7.3
124	157	54	1	3	1	5	0.16	0.10	130	139	7.5
125	159	38	6	7	5	12	0.09	0.10	110	119	7.2
126	378	6	5	140	13	210	0.08	0.00	30	35	7.6
127	629	110	45	12	302	24	0.13	0.50	150	460	7.6
128	517	170	4	21	84	34	2.70	0.10	320	445	6.7
129	564	60	23	100	160	200	0.02	0.40	20	244	8.7
130	240	55	8	11	41	16	0.07	0.70	130	170	7.6
131	275	95	5	3	7	7	0.03	0.00	250	257	7.8
132	173	50	2	14	4	21	0.55	0.00	120	134	8.3
133	364	78	8	5	20	18	6.00	0.10	204	238	7.3
134	494	85	12	26	26	21	3.10	0.00	265	267	7.1
135	418	34	31	39	72	75	7.20	1.10	130	225	7.6
136	715	148	4	38	160	29	5.50	0.00	264	395	7.0
137	388	78	9	6	10	40	8.40	0.15	194	246	7.0
138	518	99	5	37	10	83	4.00	0.15	230	274	6.9
139	379	73	13	0	33	15	4.80	0.10	189	244	7.2
140	621	124	11	23	10	49	1.50	0.20	330	357	6.8
141	419	63	34	17	170	24	0.09	0.60	110	297	7.2
142	166	24	5	2	10	8	0.10	0.15	88	105	6.6
143	718	124	6	65	10	85	0.18	0.00	350	334	6.8
144	497	35	34	44	12	128	0.10	1.30	184	277	6.6
145	360	110	3	18	21	28	0.00	0.20	256	287	7.1
146	253	46	7	10	4	12	0.06	0.40	143	143	8.4
147	150	35	9	3	2	5	0.00	0.20	122	124	7.3
148	684	142	5	31	30	39	0.01	0.00	358	375	6.9
149	228	61	2	17	13	29	0.00	0.10	138	160	7.2
150	658	64	23	85	0	75	0.50	0.50	336	285	7.4
151	258	82	4	6	18	11	0.00	0.10	200	221	7.0
152	1262	127	111	68	125	309	0.42	1.00	410	774	7.1

Table 6. Continued

Obs	TDS	CA	MG	NA	SO4	CL	FE	F	ALK	HARD	PHI
183	436	80	14	74	91	110	0.00	0.4	116	182	7.9
184	819	130	16	73	5	104	0.35	0.2	402	391	7.8
195	483	42	38	53	120	88	0.00	1.2	135	261	7.5

Table 7. Mean Values and Range of the Analytical Parameters for 155 Florida Water Samples

Parameter*	Mean	Range
TDS	456	44-1,774
Ca	71	4-260
Mg	16	0-111
Na	47	0-403
Cl	91	3-910
SO ₄	41	0-370
Fe	0.6	0-10.5
F	0.4	0-7.5
Hard†	247	14-774
Alk†	182	11-420
pH	7.45	6.20-9.20
pH _s **	7.49	6.70-9.97

* All Values in mg/L except Hard, Alk, pH, and pH_s.

† In mg/L as CaCO₃.

** Evaluated via computer method using the quadratic pH_s equation.

Table 8. Mean Values and Range of Concentrations and Percentages of Free Ions and Ion Pairs for the 155 Florida Water Samples

Ionic Species	Concentration (Moles/l)		Percentage	
	Mean	Range	Mean	Range
Total Ca^{+2}	1.77×10^{-3}	$9.98 \times 10^{-5} - 6.49 \times 10^{-3}$		
Free Ca^{+2}	1.64×10^{-3}	$9.37 \times 10^{-5} - 5.21 \times 10^{-3}$	93.2	80.3 - 97.7
CaHCO_3^{+1}	8.15×10^{-5}	$5.94 \times 10^{-9} - 3.36 \times 10^{-4}$	4.0	<0.01 - 8.1
CaSO_4^0	5.04×10^{-5}	0	2.4	0.0 - 15.3
CaCO_3^0	2.77×10^{-6}	$1.61 \times 10^{-6} - 5.72 \times 10^{-6}$	0.3	<0.01 - 5.7
CaOH^{+1}	7.42×10^{-8}	$3.11 \times 10^{-9} - 9.90 \times 10^{-6}$	<0.1	<0.01 - 1.1
Total Mg^{+2}	6.90×10^{-4}	0		
Free Mg^{+2}	6.17×10^{-4}	0	91.6	68.1 - 100.0
MgHCO_3^{+1}	2.23×10^{-5}	0	3.1	0.0 - 6.7
MgSO_4^0	4.92×10^{-5}	0	4.9	0.0 - 28.7
MgCO_3^0	1.82×10^{-6}	0	0.2	0.0 - 5.1
MgOH^{+1}	3.09×10^{-8}	0	<0.02	0.0 - 0.9
Total Na^{+1}	2.02×10^{-3}	0		
Free Na^{+}	2.00×10^{-3}	0	98.9	92.2 - 100.0
NaHCO_3^0	3.38×10^{-6}	0	0.2	0.0 - 0.3
NaSO_4^{-1}	2.50×10^{-5}	0	0.9	0.0 - 7.6
NaCO_3^{-1}	1.23×10^{-7}	0	<0.01	0.0 - 0.1

pairs were mainly in the form of NaSO_4^- and NaHCO_3^0 with insignificant quantities of NaCO_3^- . The low percentage of Na ion pairs indicate they are not important in affecting the ionic interaction in the system or the total ionic strength of the water. Very low concentrations of sodium ion pairs in natural waters have been reported by other workers (58).

Compared to sodium, the other two major cations, calcium and magnesium, formed significant concentrations of ion pairs. The calcium ion pair concentration averaged almost 7% of the total calcium concentration. This compared closely to the 5% ion pair level estimated by Stumm and Morgan (72) for natural waters. The calcium ion pairs were primarily in the form of CaHCO_3^+ and CaSO_4^0 . The concentrations of CaCO_3^0 and CaOH^+ were insignificant over the pH range of 6.20 to 9.20 of the water samples. These ion pairs may be significant at higher pH. With a pH increase, the ionization of HCO_3^- would be shifted in favor of CO_3^{2-} formation. Thus, more CaCO_3^0 would be produced because more CO_3^{2-} ions would be present to interact with Ca^{+2} ions. Likewise, at higher pH, especially beyond pH 10.0, the OH^- concentration starts to predominate. This energetically favors ion pairing between Ca^{+2} and OH^- ions. Sturrock et al. (74) reported that the CaOH^+ concentration becomes important in the pH range 10 to 12. This was determined as a result of equilibrium studies on CaCO_3 precipitation in water softening systems.

Only MgHCO_3^+ and MgSO_4^0 appear important in the ionic speciation of magnesium ions. However, the concentration of MgSO_4^0 generally is slightly higher than the concentration of MgHCO_3^+ . The mean percentage of the total magnesium concentration of MgSO_4^0 is 4.9% compared to 3.1% for MgHCO_3^+ . Together they constitute an average of 8.0% of the total Mg^{+2} quantities. The level of the other ion pairs, MgCO_3^0 and MgOH^+ , is very low and is insignificant as far as ion pairing is concerned. Again, it would be expected that the hydroxide and carbonate ion pairs of magnesium would predominate at very high pH values, which are outside the pH range of most water supplies.

Figures 10 and 11 show frequency bar diagrams of the % total calcium ion pairs and % total magnesium ion pairs. The % total cation pairs indicate the fraction of the combined amounts of ion pairs of the total cation concentration. For example, the combined concentrations of CaHCO_3^+ , CaSO_4^0 , CaCO_3^0 , and CaOH^+ would be equal to the total calcium ion pairs. For magnesium ion pairs, it would be the sum of MgHCO_3^+ , MgSO_4^0 , MgCO_3^0 , and MgOH^+ . About 85% of the 155 water samples have % total Ca^+ ion pair concentrations equal to or less than 8%. The remaining 19% of the waters have the % total Ca^{+2} ion pairs ranging from 11% to 20%.

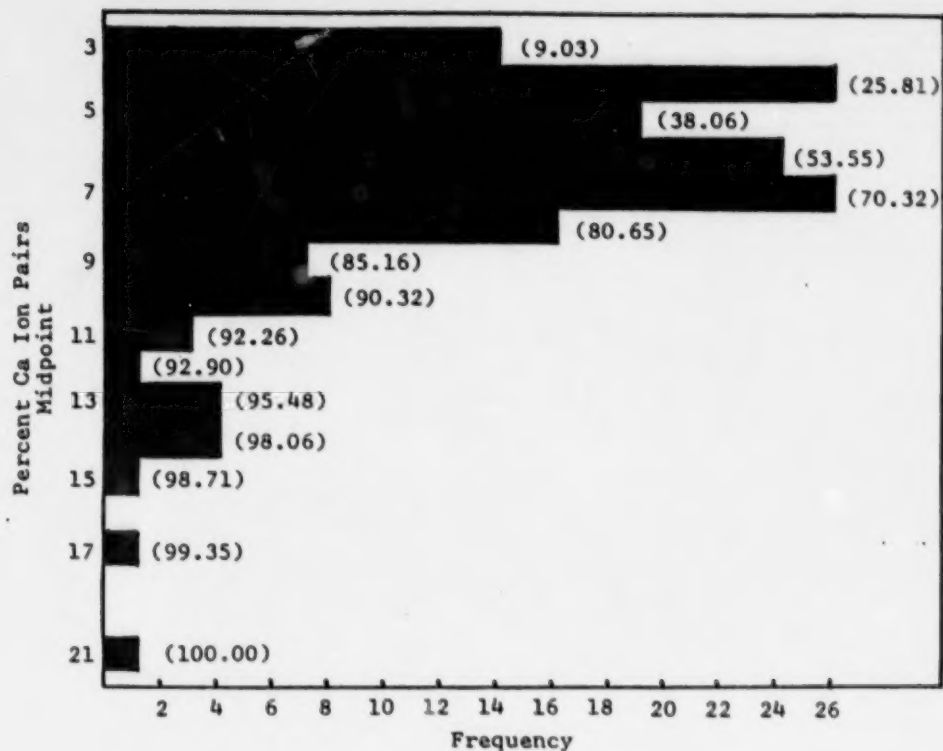


Figure 10. Frequency Bar Chart of the Percent Total Ca Ion Pairs.
Numbers Inside the Parenthesis Refer to Cumulative Percentage.

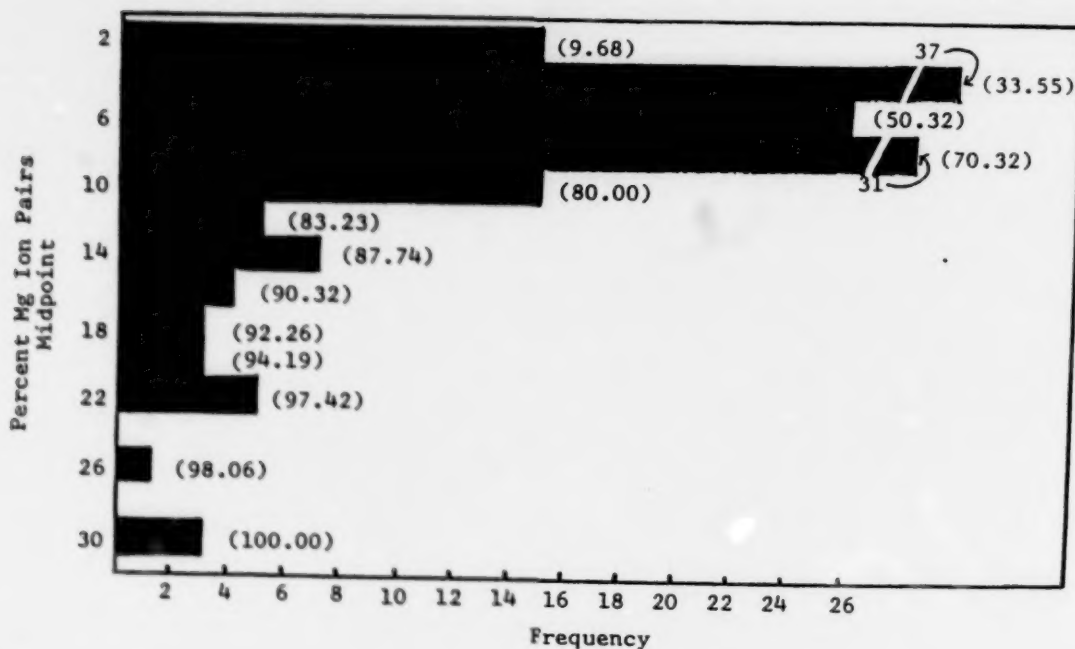
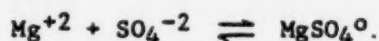
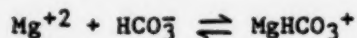
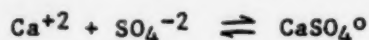
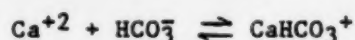


Figure 11. Frequency Bar Chart of the Percent Total Mg Ion Pairs. Cumulative Percentage is Indicated by the Numbers Inside the Parenthesis.

On the other hand, 80% of the waters have % Mg^{+2} ion pairs equal to or less than 10%. The remaining 20% of the water samples contained Mg^{+2} ion pairs which range from 11% to 20%. Therefore, the extent of ion pairing is higher for Mg^{+2} than that for Ca^{+2} . Ion pairs of both cations increase with increasing alkalinity and sulfate content of the waters. This equilibrium chemical behavior is consistent with the Le Chatelier principle involving the law of mass action which explains the increased product formation by increasing the reactant concentration so as to maintain the equilibrium. In this particular case, the following ion pair reactions



would be favored as written if the concentrations of the reacting ionic species increase. To check whether this is so, the % of bicarbonate and sulfate ion pairs of calcium and magnesium were plotted against the total sulfate concentration and total alkalinity, the latter parameter being a measure of bicarbonate concentration. Preliminary calculation showed that the HCO_3^- concentration and alkalinity are numerically equal, hence, using alkalinity in place of HCO_3^- appears justifiable. Figures 12 and 13 show the results. There is a strong linear relationship between the % $CaHCO_3^+$ and total alkalinity and between % $CaSO_4^0$ and total sulfate. Correlation coefficients of 0.95 and 0.96 were obtained for the % $CaHCO_3^+$ - alkalinity and % $CaSO_4^0$ - sulfate plot. This means that as the alkalinity and total sulfate content increase, the $CaHCO_3^+$ and $CaSO_4^0$ correspondingly increase. A comparable linear relationship was also found for Mg ion pairs. The correlation coefficient between % $MgHCO_3^0$ and alkalinity and between % $MgSO_4$ and total sulfate, respectively, is 0.88 and 0.96. This again emphasizes that increase of alkalinity and total sulfate favors formation of more bicarbonate and sulfate ion pairs of magnesium.

The calculation of the correlation coefficients between % Mg or % Ca ion pairs and alkalinity or sulfate give different results. There was a poor correlation between % $CaHCO_3^+$ and total Ca^{+2} and between % $CaSO_4^0$ and total Ca^{+2} as evidenced by the respective r values of 0.60 and 0.25. The same situation existed between % $MgHCO_3^+$ and total magnesium with $r = 0.21$ and between % $MgSO_4^0$ and total magnesium with $r = 0.31$. The weak

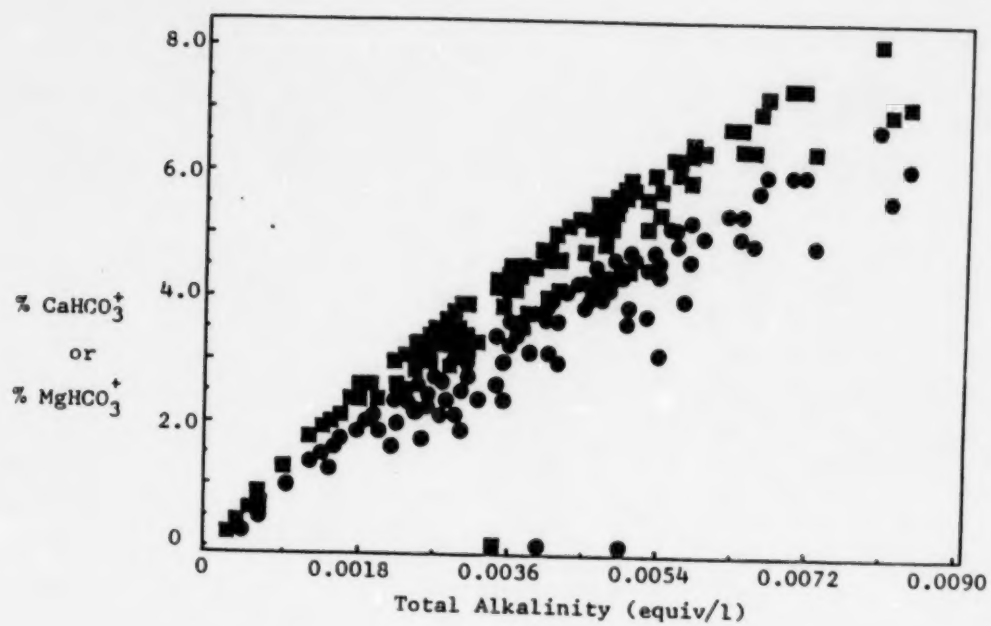


Figure 12. Relationship of % of CaHCO_3^+ (■) and % MgHCO_3^+ (●) with Total Alkalinity. The Correlation Coefficients are:
 r (■) = 0.95 and r (●) = 0.88.

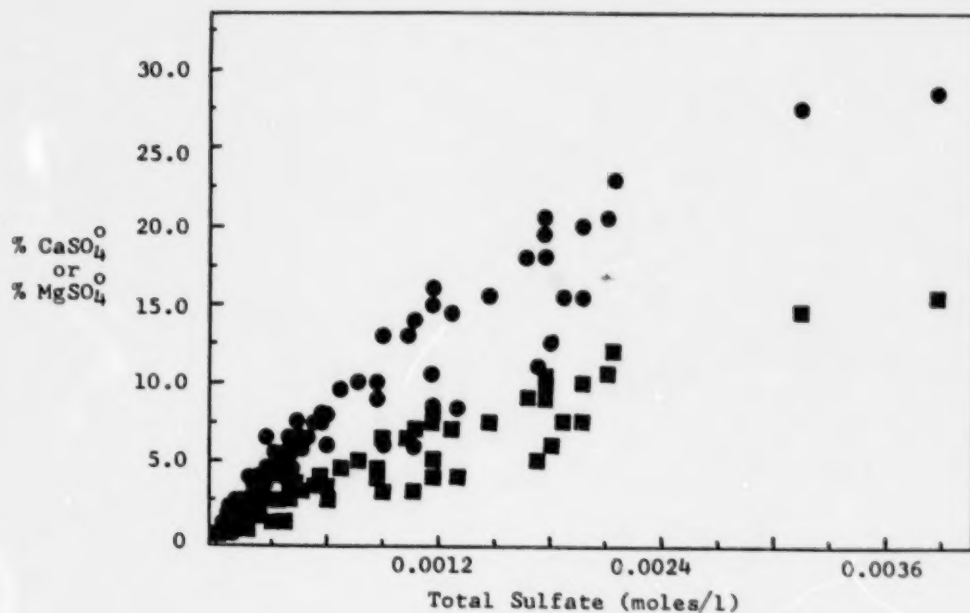


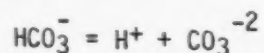
Figure 13. Relationship of % of CaSO_4 (■) and % MgSO_4 (●) with Total Sulfate. The Correlation Coefficients are:
 r (■) = 0.96 and r (●) = 0.96.

relationships obtained indicate that the complexing anions assume major importance in ion pairing since the concentrations of the ion pairs would then be a function of the bicarbonate ions from total alkalinity and from sulfate ions.

Effect of Water Quality Parameters on pH_s

As calculated from the quadratic equation, the pH_s is inherently a function of all the analytical parameters which directly relate to the $CaCO_3$ saturation. TDS appears to be an important variable in that it is related to the ionic strength of the solution which was used in the evaluation of activity and activity coefficients of ions. Since the total concentration of all ions determines the ionic strength, each ionic species such as Ca^{+2} , Mg^{+2} , Na^{+2} , SO_4^{-2} , HCO_3^- , CO_3^{-2} , and Cl^- are important in the pH_s evaluation. In addition, the pH and Alk of the water are necessary for determining the concentration of the bicarbonate species.

Even though all the analytical parameters for each water have been utilized in the pH_s calculation, it is important to evaluate how each analytical variable influences pH_s . Consequently, pH_s was plotted against each variable to determine graphically the variation of pH_s with respect to each parameter. Hardness was omitted because it is a function of two variables, calcium and magnesium, and to a lesser extent other bivalent or trivalent ions such as iron. Figures 14 and 15 illustrate the trend of pH_s with respect to each analytical variable. Only pH_s vs F^- and pH_s vs pH do not show negative linear relationships. Alkalinity and total calcium concentration are the most important factors that affect pH_s , as indicated by the values of the correlation coefficients. For pH_s vs. alkalinity, the correlation coefficient is -0.81 and for pH_s vs. Ca, the coefficient is -0.80. These results of correlation analysis are consistent with the chemical concept that the concentration of the reactants exert the predominant effect in shifting an equilibrium reaction from one direction to another. In this particular case, the total Ca^{+2} concentration is the source of free Ca^{+2} while the alkalinity at a given pH controls the availability of CO_3^{-2} which could interact with Ca^{+2} to form $CaCO_3$. As alkalinity increases, the HCO_3^- concentration correspondingly increases, which would shift the dissociation of bicarbonate in favor of carbonate ions according to the reaction.



Therefore, the pH_s would decrease with increase in alkalinity. In the same manner, an increase in Ca^{+2} concentration would lead to a pH_s drop. The pH_s decrease is an indirect reflection of the increase of calcium and

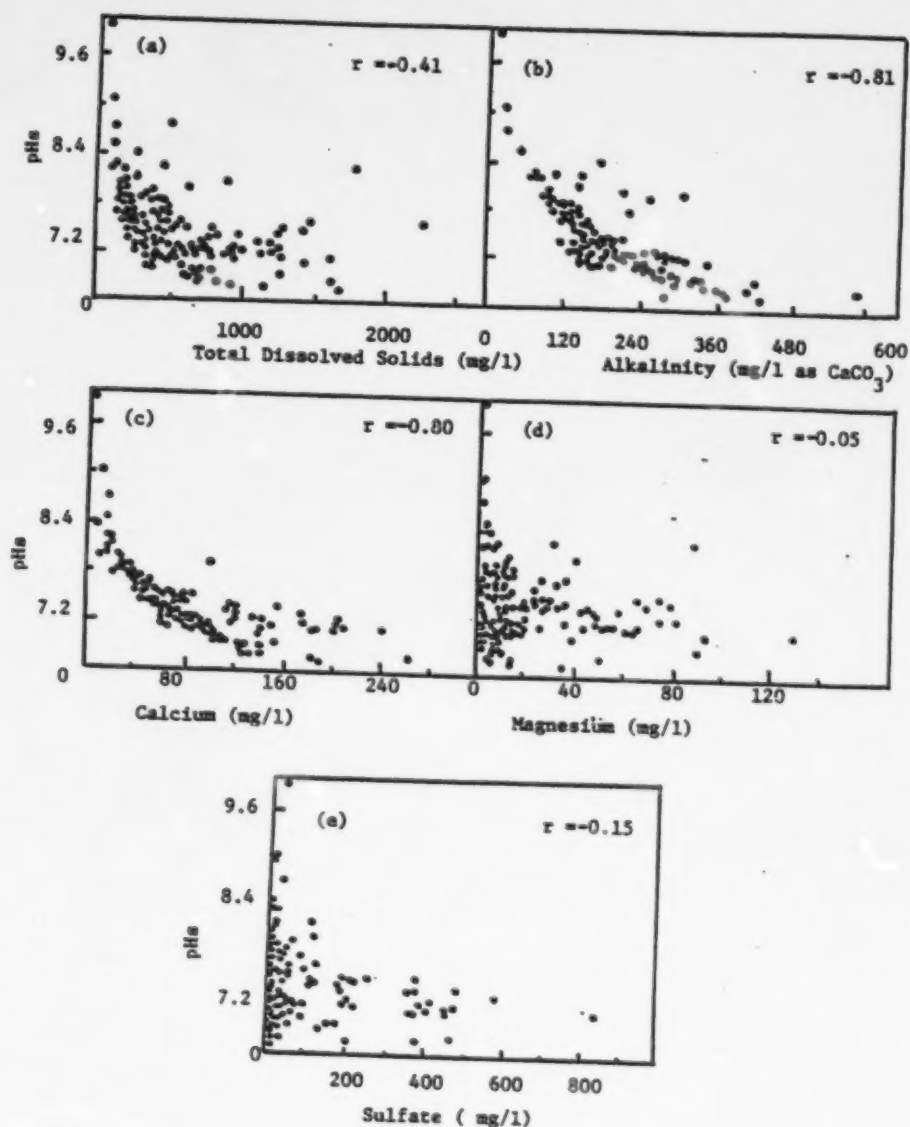


Figure 14. Variation of Quadratic pHs with (a) Total Dissolved Solids, (b) Total Alkalinity, (c) Total Calcium, (d) Total Magnesium, and (e) Total Sulfate. The Value of r in Each Graph Refers to the Correlation Coefficient.

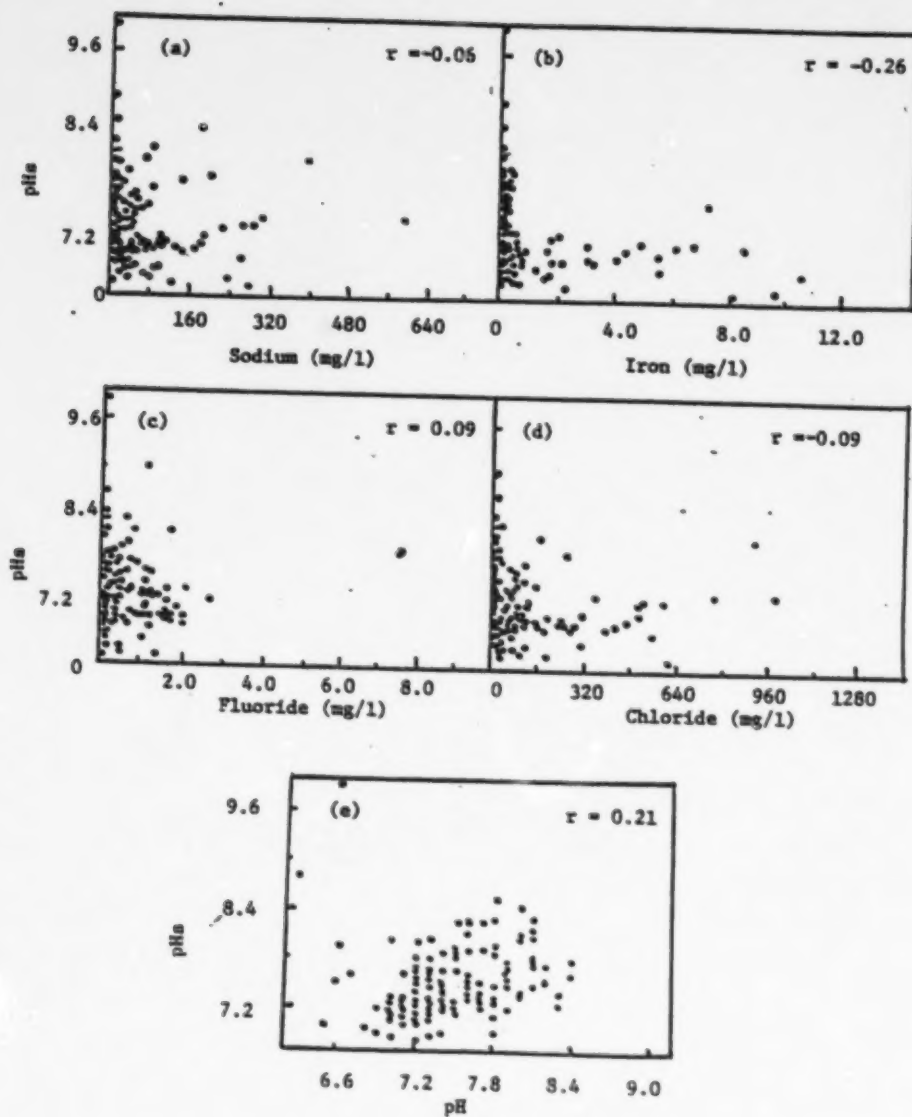


Figure 15. Variation of Quadratic pHs with (a) Sodium, (b) Iron, (c) Chloride, (d) Fluoride, and (e) pH. The Correlation Coefficient is Indicated by r .

and alkalinity because the values of these two parameters are expressed as the negative logarithmic functions when the pH_s is calculated. As an illustration, an increase in alkalinity from 1×10^{-4} equiv/L to 1×10^{-3} equiv/L is translated to a change in the negative logarithmic values from 4 to 3. If the calcium concentration is raised from 1×10^{-5} to 1×10^{-4} moles/l, this will be equal to a change in the negative logarithms from 5 to 4 or one unit drop in pH_s .

Statistical Models for Predicting the pH of $CaCO_3$ Saturation

It is common knowledge that not all water treatment plants are equipped with or have access to computers which could be utilized to evaluate pH_s and thus the $CaCO_3$ saturation index of the water. Hence, simpler ways of calculating the pH of $CaCO_3$ saturation have to be devised with the intent of arriving at a value close enough to that derived from the more complex chemical model requiring computer analysis. Several mathematical models were then constructed and tested for prediction of the equilibrium or quadratic pH_s values of the 155 water samples. Multiple regression analyses were used to analyze the empirical relationships between the dependent variable pH_s and several independent variables which correspond to the measured water quality parameters. The squared multiple correlation coefficient, R^2 , also known as the coefficient of multiple determination (75), was evaluated for each model. The value of R^2 serves as a summary measure to judge the fit of the model to a given body of data (76). It basically indicates the proportion of total variation in the dependent variable that is explained by a combination of several independent variables (75,77,219). Patterned after Kleinbaum and Kupper (78) the R^2 formula used for determining the strength of the association between the equilibrium pH_s and the best-fitting combination of independent analytical variable is

$$R^2_{pH_s/X_1, X_2, \dots, X_a} = \frac{\sum_{i=1}^n \left\{ (pH_s)_e - \overline{(pH_s)_e} \right\}^2 - \sum_{i=1}^n \left\{ (pH_s)_e - (pH_s)_p \right\}^2}{\sum_{i=1}^n \left\{ (pH_s)_e - (pH_s)_p \right\}^2}$$

where $X_1, X_2, \dots, X_a$ = independent analytical variables in the model,

$(pH_s)_e$ = equilibrium pH_s value calculated using the quadratic pH_s equation,

$\overline{(pH_s)_e}$ = mean of $(pH_s)_e$ values, and

$(pH_s)_p$ = pHs value predicted by the multiple regression model.

Three types of statistical models were constructed: linear combination, inverse function, and logarithmic function. The fit of each model was tested with the data from the 155 water samples. The multiple regression analyses were done using the Statistical Analysis Systems (SAS) by utilizing the facilities of the Northeast Regional Data Center of the State University System of Florida.

Linear Combination Model

The first model that was tested was a linear combination of three variables: calcium, alkalinity, and pH. Although the fit of the model was quite satisfactory, only about 76% of the variability in pHs could be accounted for by the regression equation. Replacing pH by total dissolved solids (TDS) in the three-variable model did improve the model fit significantly, as evidenced by a R^2 value of 0.780. Because Mg has been known to influence $CaCO_3$ precipitation by ionic substitution of Ca^{+2} ion by Mg^{+2} ion in the calcite crystal lattice, Mg was included in the third model shown in Table 9. In addition, the interaction of the two variables, Ca and Mg, was incorporated. The results showed, however, that the model was not satisfactory and could not explain 24% of the variability in pHs.

Another model was tried which defined pHs as a function of TDS, Ca, Mg, Alk, SO_4 , Cl, and pH. Even with seven variables, the value of R^2 did not improve enough. Twenty percent (20%) of the variation in pHs was still unaccounted for. When all of the analytical variables that were measured were included in the model, R^2 did not change. The encompassing model could only explain about 80% of the variation in pHs. This indicated the limitation of the linear combination models. The pH of $CaCO_3$ saturation cannot, therefore, be expressed with sufficient accuracy in terms of a linear combination of the water quality parameters.

Inverse Function Models

Table 10 lists the best inverse function models tested for predicting pHs. The first model, which included the reciprocal values to TDS, Ca, and Alk, could only explain about 78% of the value of pHs. When TDS was omitted and hardness (Hard) and SO_4 were incorporated, the model fit to the data did not change as indicated by $R^2 = 0.790$. In the third model, TDS and Mg were added. The value of R^2 was increased to 0.812. This slight increase, however, cannot be taken as a significant improvement because the model could not account for 19% of the value of pHs. There was some improvement when hardness (Hard) was added to the third model. In this six-variable inverse function model, 87% of the variability in pHs could be

explained by the predictive equation. The fit of this last model was better than any of those that resulted using the linear combination models presented in Table 9. Nevertheless, the unexplained 13% variation is still quite high and could not be easily justified as falling within the limit of experimental error, which should not amount to more than 5 to 10%. Hence, a linear combination of the reciprocal of the important water quality parameters did not predict the pHs adequately.

Table 9. Linear Combination Models for Predicting the pH of CaCO₃ Saturation

Mathematical Model	R ²
(1) $\text{pHs} = \alpha_0 + \alpha_1 \text{Ca} + \alpha_2 \text{Alk} + \alpha_3 \text{pH}$	0.775
(2) $\text{pHs} = \alpha_0 + \alpha_1 \text{TDS} + \alpha_2 \text{Ca} + \alpha_3 \text{Alk}$	0.780
(3) $\text{pHs} = \alpha_0 + \alpha_1 \text{Ca} + \alpha_2 \text{Mg} + \alpha_3 \text{Alk} + \alpha_4 (\text{Ca.Mg})$	0.760
(4) $\text{pHs} = \alpha_0 + \alpha_1 \text{TDS} + \alpha_2 \text{Ca} + \alpha_3 \text{Mg} + \alpha_4 \text{Alk} + \alpha_5 \text{SO}_4 + \alpha_6 + \alpha_7 \text{pH}$	0.805
(5) $\text{pHs} = \alpha_0 + \alpha_1 \text{TDS} + \alpha_2 \text{Ca} + \alpha_3 \text{Mg} + \alpha_4 \text{Hard} + \alpha_5 \text{Alk} + \alpha_6 \text{SO}_4 + \alpha_7 \text{Cl} + \alpha_8 \text{Na} + \alpha_9 \text{F} + \alpha_{10} \text{pH}$	0.806

Table 10. Inverse Function Models for Predicting the pH of CaCO_3 Saturation

Mathematical Model	R^2
(1) $\text{pHs} = \beta_0 + \beta_1 (\text{TDS})^{-1} + \beta_2 (\text{Ca})^{-1} + \beta_3 (\text{Alk})^{-1}$	0.785
(2) $\text{pHs} = \beta_0 + \beta_1 (\text{Ca})^{-1} + \beta_2 (\text{SO}_4)^{-1} + \beta_3 (\text{Alk})^{-1} + \beta_4 (\text{Hard})^{-1}$	0.790
(3) $\text{pHs} = \beta_0 + \beta_1 (\text{TDS})^{-1} + \beta_2 (\text{Ca})^{-1} + \beta_3 (\text{Mg})^{-1} + \beta_4 (\text{SO}_4)^{-1} + \beta_5 (\text{Alk})^{-1}$	0.812
(4) $\text{pHs} = \beta_0 + \beta_1 (\text{TDS})^{-1} + \beta_2 (\text{Ca})^{-1} + \beta_3 (\text{Mg})^{-1} + \beta_4 (\text{SO}_4)^{-1} + \beta_5 (\text{Alk})^{-1} + \beta_6 (\text{Hard})^{-1}$	0.873

Logarithmic Models

When logarithmic models were tested, satisfactory R² values were obtained. Table 11 shows that the first model composed of the logarithmic values of Ca and Alk could explain almost 96% of the variance in pHs. Inclusion of two more variables such as Cl and SO₄ slightly improved the model fit as indicated by a R² value of 0.977 of the second model. No significant difference was found when Cl was replaced by Mg as shown in the third model. Similar results were obtained when TDS was added to have five-variable logarithmic models represented by the last two predictive equations for pHs in Table 11. Only about 2% of the variance in pHs could not be accounted for by the last two mathematical models which showed a very good fit of the models to the data.

The predictive equations representing models (3) and (5) of Table 11 were chosen as the best logarithmic models. Both models contain the logarithmic values of Ca and Alk and other water quality parameters which are included in evaluation of the equilibrium pH of CaCO₃ saturation using the quadratic pHs formula. Equations (28) and (29) completely describe the mathematical models (3) and (5), respectively, and give the values of the intercept and regression coefficients.

$$\begin{aligned} \text{pHs} = & 11.207 - 0.916 \log(\text{Ca})_t + 0.039 \log(\text{Mg})_t \\ & - 0.991 \log(\text{Alk})_t + 0.032 \log(\text{SO}_4)_t \end{aligned} \quad (28)$$

$$\begin{aligned} \text{pHs} = & 11.017 + 0.197 \log(\text{TDS}) - 0.995 \log(\text{Ca})_t \\ & - 0.016 \log(\text{Mg})_t - 1.041 \log(\text{Alk})_t + 0.021 \log(\text{SO}_4)_t \end{aligned} \quad (29)$$

where (Ca)_t, (Mg)_t, and (SO₄)_t = total or analytical concentration of the given ion in mg/L,

(TDS) = total dissolved solids in mg/L, and

(Alk)_t = total or measured alkalinity in mg/L,
as CaCO₃.

As the coefficients imply, the measured total alkalinity and total calcium exert the major influence on the pH of CaCO₃ saturation. According to equation (28) the coefficient of log Ca suggests a certain portion of the logarithm of the total calcium concentration is important in evaluating pHs. The last two factors in equation (28) play significant roles if the level of magnesium and sulfate in the water are high because extensive ion pairing could take place between Mg⁺² and the anions, HCO₃⁻ and CO₃⁻², and between Ca⁺² and SO₄⁻², thereby decreasing the activities of the free

Table 11. Logarithmic Function Models* for Predicting the pH of CaCO_3 Saturation.

Mathematical Model	R^2
(1) $\text{pHs} = \delta_0 + \delta_1 \log \text{Ca} + \delta_2 \log \text{Alk}$	0.959
(2) $\text{pHs} = \delta_0 + \delta_1 \log \text{Ca} + \delta_2 \log \text{Alk}$ $+ \delta_3 \log \text{SO}_4 + \delta_4 \log \text{Cl}$	0.976
(3) $\text{pHs} = \delta_0 + \delta_1 \log \text{Ca} + \delta_2 \log \text{Mg}$ $+ \delta_3 \log \text{Alk} + \delta_4 \log \text{SO}_4$	0.974
(4) $\text{pHs} = \delta_0 + \delta_1 \log \text{TDS} + \delta_2 \log \text{Ca}$ $+ \delta_3 \log \text{Alk} + \delta_4 \log \text{Cl} + \delta_5 \log \text{pH}$	0.977
(5) $\text{pHs} = \delta_0 + \delta_1 \log \text{TDS} + \delta_2 \log \text{Ca}$ $+ \delta_3 \log \text{Mg} + \delta_4 \log \text{Alk} + \delta_5 \log \text{SO}_4$	0.978

*All values of the independent variables in each model are exposed as $\log_{10}$.

Ca^{+2} and CO_3^{-2} ions. In addition, increasing quantities of Mg^{+2} and SO_4^{-2} would increase the ionic strength, and consequently lower the activity coefficients of Ca^{+2} and CO_3^{-2} .

The logarithmic regression model corresponding to equation (29) indicates that in addition to Ca, Mg, Alk, and SO_4 , TDS is another important variable that affects pHs. Incorporating TDS into the model lowers the regression coefficients for $\log (\text{Mg})_t$ but with a very slight increase in R^2 value. The additional advantage of this last model is that it defines pH as a function of Ca, Mg, Alk, and SO_4 , which are all related to the solubility equilibrium and ion pair formation that affects CaCO_3 stability and of TDS which is related to the ionic strength.

The predictive expressions represented by equations (28) and (29) may be converted into nonlinear forms which will define the activity of hydrogen ion at calcium carbonate saturation. Thus, equation (28) becomes

$$\{H_s^+\} = \frac{(\text{Ca})_t^{0.916} (\text{Alk})_t^{0.991}}{(10^{C_1}) (\text{Mg})_t^{0.039} (\text{SO}_4)_t^{0.032}}$$

where $C_1 = \text{constant} = 11.207$

Equation (29) is now transformed to

$$\{H_s^+\} = \frac{(\text{Ca})_t^{0.995} (\text{Alk})_t^{1.041} (\text{Mg})_t^{0.016}}{(10^{C_2}) (\text{TDS})^{0.197} (\text{SO}_4)^{0.021}}$$

In both nonlinear expressions the hydrogen ionic activity is directly proportional to calcium concentration and alkalinity. This implies that any increase of either one or both water quality parameters correspondingly increase the hydrogen ionic activity and results to a lower pH_s value.

There is one interesting point that the best two logarithmic models imply in connection with the CaCO_3 saturation model presented in this study. Of the 11 ion pairs that were considered in the chemical model, only ion pairs of Ca^{+2} in the form of CaHCO_3^+ and CaSO_4^0 and of Mg^{+2} in the form of MgHCO_3^+ and MgSO_4^0 , are important in the equilibrium speciation evaluation. Increase in sulfate content was found to increase ion pairing. Wigley (79) reported that as much as 27% of the total calcium in some natural waters could be tied up in ion pairs with sulfate. However, Stumm and Morgan (72) believe that complex and ion pair formation is of little importance in most fresh waters. They estimated that the bicarbonate or carbonate complexes of Ca^{+2} do not exceed 5% of the total calcium concentration. The results of the present study indicate that with increased concentrations of HCO_3^- , Mg^{+2} , and SO_4^{-2} , significant ion pair formation is thermodynamically possible. This would affect the CaCO_3 solubility equilibrium as well as the evaluation of the pH of CaCO_3 saturation. For the 155 water samples an average of about 7% of the total calcium was found to be in the form of ion pairs under equilibrium conditions.

This average value is slightly higher than the value estimated by Stumm and Morgan (72) because the bicarbonate and sulfate complexes were included in the present equilibrium calculation. The sulfate complexes were not considered by Stumm and Morgan. Water with high sulfate content can yield CaSO_4^0 complex comprising as much as 15% of the total calcium concentration, as shown in Table 8 and in the frequency bar chart in Figure 10.

Comparison of pHs Values Obtained from the Different Calculation Methods

To assess the accuracy of the best two logarithmic models for predicting the pH of CaCO_3 saturation, the models were used in determining the pHs of the 155 Florida water samples, the chemical compositions of which are presented in Table 6. The pHs values of the water samples were similarly calculated using the quadratic and simplified pHs equations that have been derived in Chapter Six. Another computer program, WATSPEC2 (80) was also used for the calculation of pHs in addition to the commonly used computational method of applying the Langelier and Larson-Buswell equations. In addition the graphical procedure with the aid of the Caldwell-Lawrence diagrams was used. WATSPEC2 is an updated version of WATSPEC that was originally reported by Wigley (79). This computer program was expanded by the U.S. Environmental Protection Agency (EPA) workers in Cincinnati at the same time a comparable program was being revised and modified for the equilibrium speciation calculation using the quadratic pHs formula developed in the present study. For identification purposes, the computer program for evaluating equilibrium pHs using the quadratic

equation was named N77 Corrosion Project program.

The symbols listed in Table 12 were used to define the pHs values obtained by the different calculation methods. The same abbreviated

Table 12. Names of the pHs Values to Which the Calculation Procedures were Associated

Name	Meaning	Calculation Method Using
SIMPHS	Simplified pHs	Equation (27)
QUAPHS	Quadratic pHs	N-77 Computer Program
WSP2PHS	WATSPEC2 pHs	WATSPEC2 Computer Program
STA4PHS	pHs from Statistical four-variable model	Equation 28
STA5PHS	pHs from Statistical five-variable model	Equation 29
LANGPHS	Langelier pHs	Langelier's equation
LARBPHS	Larson-Buswell pHs	Larson-Buswell equation
CDLWPHS	Caldwell-Lawrence pHs	Water Conditioning Diagrams

names will be referred to in the subsequent discussion and tabulation of the pHs values. Both QUAPHS and WSP2PHS yield pHs values evaluated through computer calculation under equilibrium conditions. The differences are that more ion pairs were considered in the WSP2PHS method than those in the QUAPHS calculation and some values of the association and thermodynamic constants in both programs are different. In the WATSPEC2 program concentrations of ionic species are expressed in molality, while in the N77 Corrosion Research program for computing QUAPHS, the concentrations are in molarity. The value of the calcite solubility product and equilibrium constants used in the QUAPHS calculation were also used in the evaluation of the Langelier and Larson-Buswell pHs values instead of those originally utilized by the proponents. The graphical approximation of pHs via Caldwell-Lawrence diagrams were done using water conditioning diagrams at 25°C and TDS value close to the TDS of the water sample. For instance, a

Caldwell-Lawrence diagram at 25°C and TDS = 400 mg/l was used for a water with a TDS of 600 mg/l. Only 25°C temperature was considered since the temperature of the water samples range from 20 to 27°C.

The results of the pHs evaluation of the 155 water samples using eight different calculation procedures are shown in Table 13. Only 137 values were reported for CDLWPHS because the calcium concentration and total alkalinity of the remaining 18 waters were outside the range of values in the water conditioning diagrams. Inspection of the pHs values reveal that generally SIMPHS, QUAPHS, WSP2PHS, STA4PHS, and STA5PHS are close to one another. LANGPHS and LARBPHS are lower compared to the pHs values obtained from the first five calculation methods. The highest values are those derived from the approximations in Caldwell-Lawrence diagrams (CDLWPHS).

To compare the pHs values more readily, plots of QUAPHS against the remaining pHs values were constructed as shown in Figures 16 and 17. This was done not only to assess the functional fit of the two best logarithmic models, STA4PHS and STA5PHS with QUAPHS more easily, but also to compare QUAPHS with LANGPHS, LARBPHS, and CDLWPHS pictorially. Data points falling on the diagonal line indicate that the two calculated pHs values shown in the graph agree very closely. Thus, the two sets of pHs values obtained via computer methods, QUAPHS and WSP2PHS, are almost equivalent. Except for a few data points, STA4PHS and especially STA5PHS values agree well with QUAPHS. Therefore, the equations describing both statistical models can be used with sufficient accuracy for calculating pHs. This is the case also with SIMPHS which yielded a good graphical fit with QUAPHS. Plots of QUAPHS vs LARBPHS and QUAPHS vs LANGPHS show that the data points generally fall above the diagonal line. The departure from the graphical fit is more conspicuous in LANGPHS than in LARBPHS. In the case of CDLWPHS, essentially all the data points lie below the diagonal line indicating that CDLWPHS values are consistently higher than the QUAPHS values.

Statistical analyses were performed to evaluate whether the pHs values obtained using the eight different computational procedures were different. The tests were done only for 137 observations because, as previously mentioned, 18 pHs values were missing for CDLWPHS. The pHs data were analyzed utilizing Statistical Analysis Systems (SAS) using the Northeast Regional Data Center of the State University System of Florida. Table 14 presents the results of the analysis of variance (ANOVA) to test whether the eight mean pHs values were statistically different. The calculated F value was sufficiently high at the 95% confidence interval. Therefore, there is reason to believe that the pHs means are significantly different. To specifically determine which mean values are the same or different, Duncan's multiple comparison test was made at a 95% confidence interval.

Table 13. Values of the pH of CaCO₃ Saturation of the 155 Water Samples. (The meanings associated with the pHs symbols are explained in Table 12)

ONS	SIMPHS	QUAPHS	WSP2PHS	STA4PHS	STA5PHS	LANGPHS	LARBPHS	CDLWPHS
1	7.12	7.19	7.15	7.18	7.15	6.84	7.03	7.57
2	7.39	7.40	7.36	7.42	7.44	7.21	7.34	7.94
3	8.97	9.05	8.93	9.02	9.03	8.88	8.95	9.68
4	7.20	7.25	7.20	7.25	7.27	6.97	7.14	7.71
5	7.13	7.19	7.15	7.19	7.18	6.86	7.06	7.62
6	7.00	7.05	7.00	7.04	7.09	6.81	6.96	7.54
7	7.78	7.82	7.77	7.85	7.84	7.60	7.74	8.36
8	7.02	7.06	7.00	7.03	7.07	6.82	6.97	7.55
9	7.22	7.26	7.21	7.28	7.28	7.03	7.18	7.71
10	6.64	6.70	6.64	6.62	6.65	6.30	6.51	
11	7.65	7.64	7.62	7.68	7.66	7.51	7.62	8.12
12	6.91	6.96	6.91	6.97	6.98	6.68	6.84	7.37
13	7.21	7.26	7.21	7.27	7.26	6.99	7.15	7.73
14	7.16	7.19	7.14	7.17	7.21	6.98	7.12	7.72
15	7.20	7.25	7.20	7.27	7.26	7.02	7.16	7.75
16	7.04	7.09	7.03	7.11	7.11	6.83	6.99	7.56
17	7.01	7.03	7.00	7.08	7.07	6.67	7.08	
18	7.28	7.32	7.30	7.34	7.35	7.11	7.25	7.85
19	8.17	8.20	8.14	8.23	8.20	8.07	8.16	8.67
20	8.19	8.23	8.35	8.22	8.25	7.99	8.14	8.75
21	7.20	7.24	7.19	7.26	7.25	7.01	7.16	7.75
22	7.39	7.44	7.42	7.46	7.45	7.18	7.34	7.92
23	7.62	7.67	7.64	7.70	7.69	7.43	7.62	8.20
24	7.79	7.81	7.76	7.83	7.81	7.67	7.77	8.25
25	7.12	7.16	7.14	7.16	7.15	6.93	7.07	7.67
26	6.84	6.89	6.83	6.88	6.89	6.60	6.77	7.33
27	7.55	7.59	7.54	7.62	7.62	7.35	7.50	8.10
28	7.03	7.07	7.01	7.04	7.10	6.83	6.96	7.57
29	7.57	7.60	7.55	7.64	7.62	7.43	7.55	
30	7.94	8.00	7.96	7.94	8.02	7.73	7.89	
31	7.85	7.88	7.83	7.93	7.87	7.72	7.83	7.91
32	7.37	7.41	7.36	7.43	7.42	7.17	7.32	7.48
33	6.96	7.01	6.95	7.02	6.98	6.76	6.91	7.70
34	7.18	7.22	7.17	7.23	7.23	6.96	7.12	7.67
35	8.18	8.21	8.15	8.25	8.20	8.07	8.17	8.67
36	6.83	6.89	6.83	6.88	6.91	6.62	6.78	7.34
37	7.37	7.43	7.39	7.45	7.43	7.13	7.30	7.88
38	7.00	7.04	6.99	7.02	7.07	6.80	6.95	7.53
39	7.04	7.09	7.03	7.09	7.10	6.84	6.99	7.57
40	7.03	7.08	7.02	7.09	7.09	6.83	6.98	7.56
41	7.22	7.25	7.20	7.29	7.27	7.03	7.17	7.77
42	7.09	7.13	7.08	7.15	7.14	6.86	7.03	7.59
43	6.93	6.97	6.93	6.96	6.97	6.71	6.87	7.44
44	7.26	7.30	7.25	7.32	7.30	7.04	7.20	7.77
45	7.35	7.40	7.36	7.38	7.40	7.03	7.23	7.93
46	7.04	7.10	7.04	7.11	7.11	6.82	6.99	7.55
47	7.62	7.65	7.61	7.67	7.67	7.41	7.56	8.17
48	8.34	8.40	8.35	8.33	8.39	8.19	8.31	8.95
49	7.48	7.53	7.48	7.46	7.51	7.15	7.36	8.01
50	7.01	7.06	7.01	7.08	7.06	6.80	6.96	7.53
51	7.13	7.18	7.13	7.18	7.17	6.87	7.05	7.60
52	7.45	7.51	7.46	7.54	7.50	7.25	7.40	7.97
53	6.88	6.96	6.90	6.94	6.96	6.63	6.81	7.37
54	7.17	7.24	7.20	7.26	7.22	6.93	7.10	7.67
55	7.41	7.47	7.43	7.48	7.47	7.16	7.33	7.90
56	6.91	6.95	6.90	6.94	6.93	6.65	6.85	7.43
57	7.41	7.48	7.44	7.49	7.48	7.18	7.35	7.92
58	7.17	7.22	7.17	7.24	7.23	6.96	7.12	7.70
59	7.94	7.97	7.91	7.98	8.00	7.81	7.92	8.40
60	6.66	6.76	6.71	6.70	6.71	6.36	6.55	7.07
61	8.14	8.17	8.12	8.21	8.21	8.02	8.12	8.62
62	7.57	7.61	7.59	7.66	7.62	7.41	7.54	8.15
63	8.22	8.25	8.20	8.28	8.26	8.11	8.21	8.72
64	7.21	7.35	7.20	7.38	7.35	7.15	7.28	7.87
65	8.04	8.08	8.03	8.09	8.10	7.89	8.01	8.70
66	8.45	8.49	8.43	8.52	8.51	8.35	8.44	8.89
67	7.90	7.98	7.93	8.01	7.98	7.84	7.94	8.43
68	7.05	7.10	7.05	7.11	7.11	6.85	7.00	7.58
69	7.44	7.49	7.46	7.48	7.48	7.17	7.36	7.92
70	7.54	7.58	7.53	7.62	7.61	7.37	7.54	8.12
71	7.77	7.82	7.77	7.82	7.82	7.50	7.73	8.36
72	7.54	7.61	7.56	7.65	7.61	7.42	7.55	8.17
73	7.98	8.04	7.99	7.97	8.04	7.71	7.90	8.28
74	7.71	7.74	7.69	7.80	7.76	7.54	7.68	8.32
75	8.17	8.24	8.19	8.10	8.21	7.92	7.04	8.34

Table 13. Continued

OBS	S IMPHS	QUAPHS	WSP2PHS	STA4PHS	STA5PHS	LANGPHS	LARBPHS	COLWPHS
76	7.52	7.55	7.50	7.59	7.55	7.37	7.50	
77	7.85	7.88	7.83	7.92	7.91	7.72	7.83	
78	7.22	7.27	7.23	7.28	7.30	6.98	7.16	7.72
79	8.01	8.04	7.99	8.09	8.06	7.87	7.98	8.47
80	7.40	7.44	7.39	7.47	7.44	7.24	7.37	7.77
81	7.96	7.99	7.95	8.03	8.03	7.84	7.94	8.38
82	7.96	7.99	7.94	8.04	8.00	7.83	7.94	8.42
83	7.72	7.75	7.71	7.79	7.79	7.57	7.69	8.36
84	7.07	7.11	7.06	7.13	7.12	6.87	7.02	7.60
85	7.68	7.71	7.69	7.73	7.72	7.53	7.66	8.30
86	7.05	7.10	7.05	7.11	7.10	6.84	7.00	7.57
87	7.80	7.83	7.78	7.85	7.83	7.65	7.77	8.40
88	7.08	7.12	7.07	7.14	7.13	6.87	7.03	7.60
89	7.67	7.69	7.65	7.68	7.73	7.52	7.67	8.28
90	7.04	7.09	7.04	7.10	7.10	6.83	7.04	7.56
91	7.39	7.42	7.38	7.47	7.45	7.21	7.35	7.95
92	7.98	8.01	7.96	8.06	8.00	7.85	7.96	8.43
93	7.39	7.42	7.35	7.47	7.45	7.20	7.34	7.95
94	7.83	7.86	7.82	7.91	7.86	7.69	7.81	
95	7.37	7.41	7.36	7.45	7.44	7.19	7.33	7.94
96	7.09	7.13	7.08	7.14	7.14	6.85	7.02	7.58
97	7.13	7.17	7.12	7.11	7.16	6.88	7.04	7.72
98	7.02	7.03	7.02	7.08	7.07	6.82	6.97	7.55
99	6.67	6.75	6.70	6.71	6.73	6.37	6.57	
100	7.58	7.62	7.59	7.64	7.65	7.38	7.53	8.14
101	7.51	7.56	7.53	7.59	7.58	7.30	7.46	8.05
102	7.41	7.45	7.40	7.49	7.44	7.24	7.39	7.98
103	7.18	7.22	7.17	7.18	7.22	6.95	7.12	7.68
104	7.39	7.45	7.41	7.40	7.45	7.08	7.29	7.75
105	7.12	7.16	7.11	7.14	7.18	6.86	7.04	7.73
106	7.13	7.18	7.13	7.19	7.19	6.94	7.09	7.67
107	7.26	7.29	7.24	7.25	7.29	7.01	7.18	7.74
108	8.69	8.75	8.67	8.79	8.76	8.59	8.68	9.38
109	7.15	7.19	7.13	7.13	7.18	6.87	7.06	7.73
110	9.61	9.97	9.57	9.62	9.66	9.37	9.61	
111	7.05	7.09	7.04	7.03	7.08	6.76	6.96	7.64
112	7.85	7.89	7.84	7.90	7.91	7.66	7.80	8.40
113	8.98	7.04	8.99	6.99	7.02	6.66	6.86	7.52
114	8.79	8.84	9.50	8.65	8.87	8.65	8.76	9.35
115	7.23	7.28	7.25	7.22	7.25	6.92	7.12	7.79
116	7.41	7.45	7.40	7.47	7.43	7.23	7.37	7.96
117	7.41	7.47	7.41	7.47	7.45	7.08	7.28	7.94
118	6.96	6.97	6.95	7.01	7.00	6.75	6.91	7.48
119	7.13	7.17	7.12	7.20	7.18	6.92	7.07	7.66
120	7.41	7.44	7.41	7.46	7.48	7.22	7.37	7.95
121	8.44	8.52	8.48	8.56	8.56	8.36	8.46	8.99
122	7.92	7.97	7.93	7.99	8.00	7.72	7.87	8.45
123	7.23	7.27	7.23	7.30	7.30	7.04	7.19	7.78
124	7.50	7.52	7.47	7.53	7.53	7.35	7.47	
125	7.72	7.74	7.69	7.79	7.76	7.57	7.69	
126	9.13	9.25	9.10	9.09	9.23	8.94	9.09	
127	7.25	7.32	7.30	7.32	7.30	6.98	7.17	7.71
128	6.71	6.76	6.72	6.79	6.76	6.46	6.64	7.19
129	8.34	8.42	8.44	8.41	8.46	8.12	8.29	8.90
130	7.52	7.55	7.51	7.60	7.57	7.35	7.48	8.10
131	7.02	7.05	7.01	7.07	7.04	6.82	6.97	7.56
132	7.57	7.60	7.57	7.62	7.61	7.42	7.54	0.00
133	7.19	7.23	7.17	7.26	7.25	7.00	7.14	7.73
134	7.05	7.10	7.04	7.13	7.12	6.85	7.00	7.58
135	7.76	7.81	7.74	7.83	7.83	7.55	7.81	8.32
136	6.86	6.94	6.88	6.91	6.94	6.61	6.94	7.34
137	7.20	7.25	7.19	7.28	7.27	7.02	7.17	7.76
138	7.05	7.09	7.04	7.10	7.12	6.84	7.00	7.57
139	7.24	7.29	7.24	7.34	7.31	7.06	7.21	7.79
140	6.81	6.87	6.81	7.87	5.87	6.59	6.75	7.32
141	7.54	7.64	7.60	7.67	7.64	7.35	7.52	8.11
142	7.85	7.88	7.83	7.94	7.92	7.72	7.83	8.31
143	6.80	6.85	6.79	6.83	6.86	6.56	6.73	7.29
144	7.41	7.45	7.39	7.45	7.46	7.19	7.35	7.93
145	6.94	7.00	6.95	7.01	7.00	6.75	6.91	7.48
146	7.54	7.56	7.55	7.60	7.59	7.38	7.51	8.13
147	7.71	7.74	7.69	7.77	7.73	7.57	7.68	
148	6.73	6.79	6.73	6.78	6.80	6.49	6.66	7.22
149	7.44	7.47	7.42	7.50	7.50	7.27	7.41	8.00
150	7.09	7.14	7.08	7.10	7.12	6.86	7.03	

Table 13. Continued

OBS	SINPHS	QUAPHS	WSP2PHS	STA4PHS	STA5PHS	LANGPHS	LARBPHS	CDLWPHS
151	7.17	7.21	7.15	7.24	7.21	6.99	7.13	7.72
152	6.80	6.88	6.83	6.84	6.83	6.48	6.69	
153	7.65	7.69	7.65	7.71	7.72	7.44	7.60	8.20
154	6.73	6.79	6.74	6.76	6.77	6.48	6.64	
155	7.67	7.72	7.68	7.74	7.73	7.45	7.61	8.20

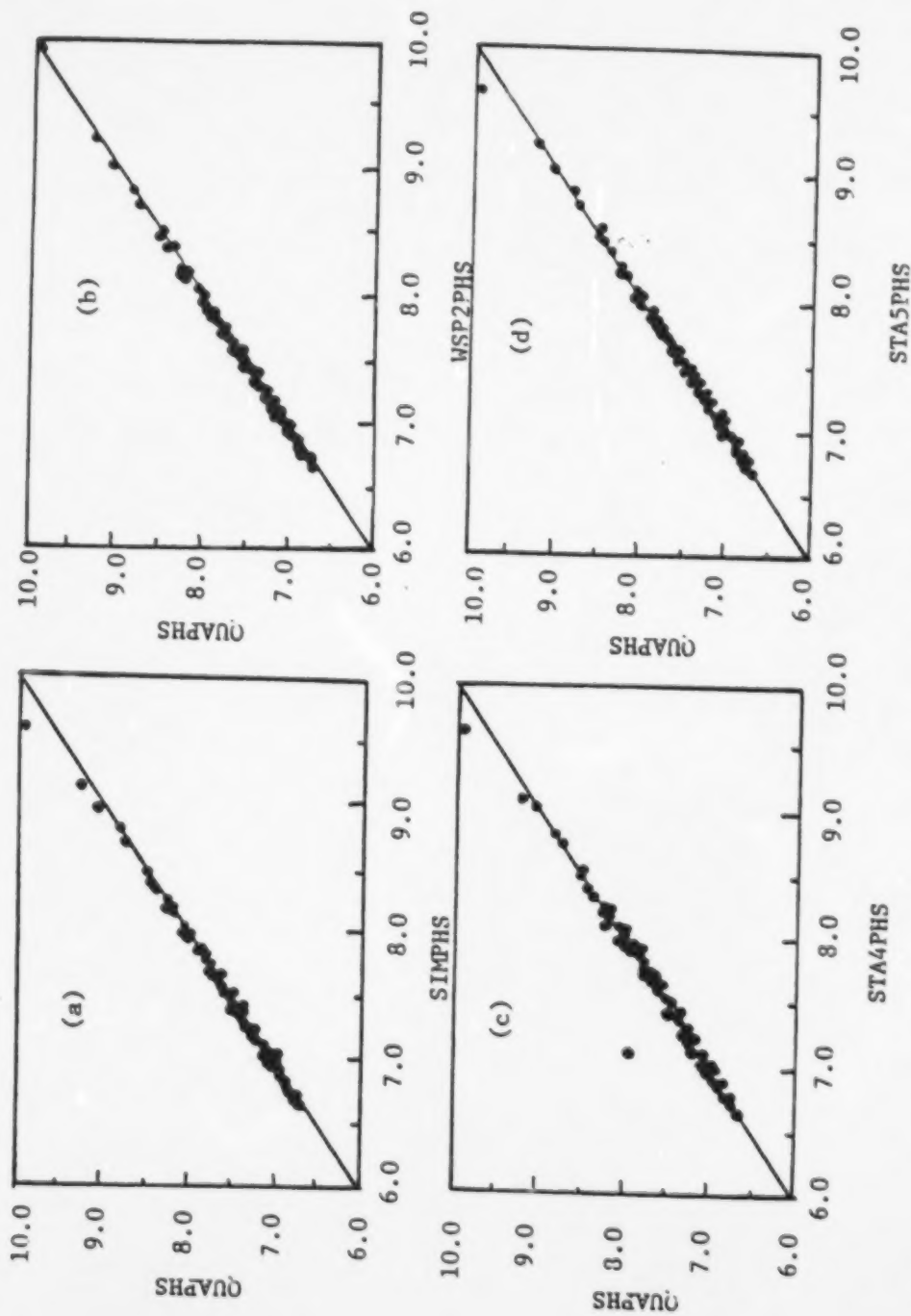


Figure 16. Graphical Comparison of the pHs Values Obtained Using the Quadratic Equation (QUAPHS) with Those Using (a) Simplified Equation (SIMPHS), (b) WATSPEC2 Computer Program (WSP2PHS), (c) Four-Variable Logarithmic Model (STA4PHS) and (d) Five-Variable Logarithmic Model (STA5PHS).

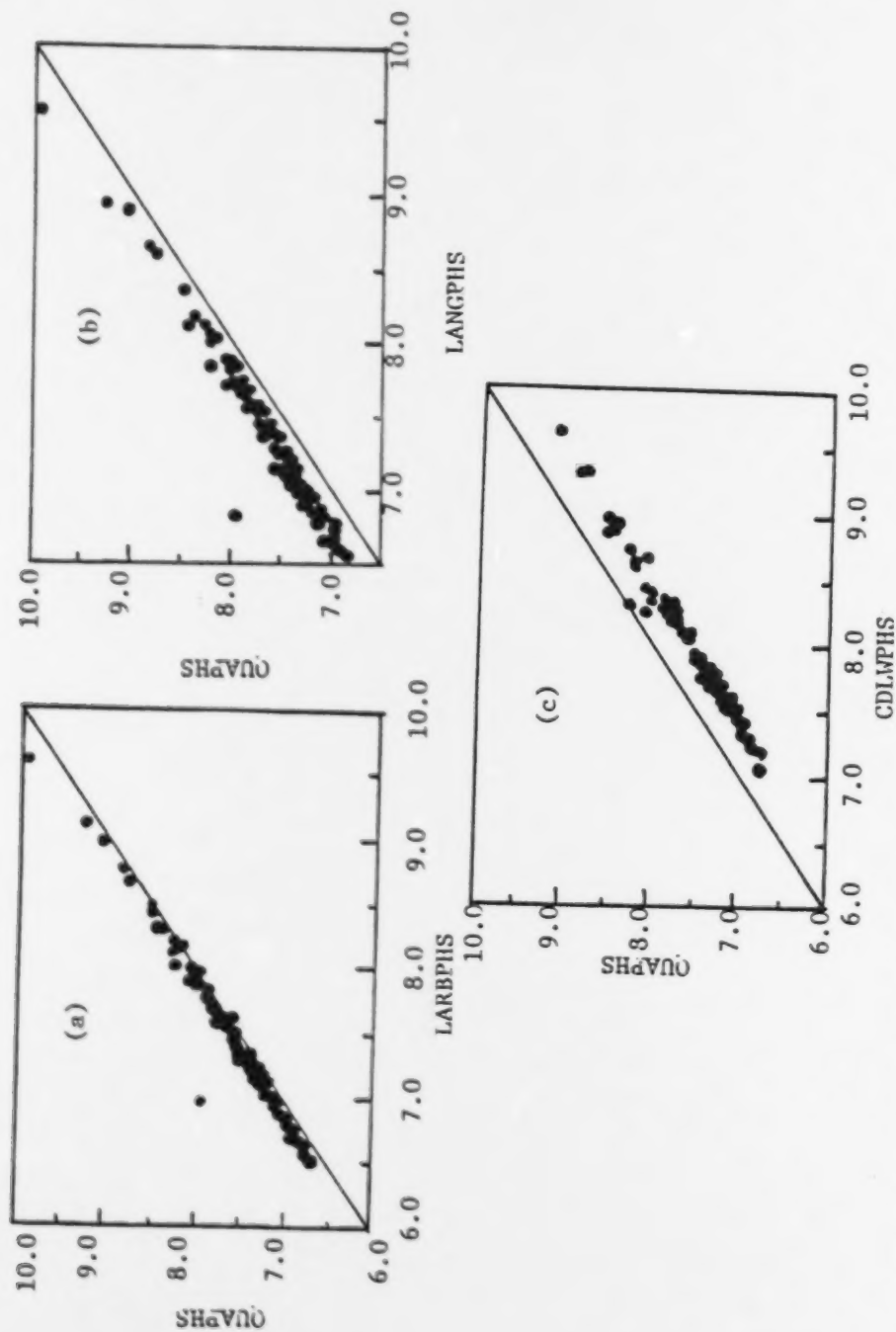


Figure 17. Graphical Comparison of the pH Values Obtained Using the Quadratic Equation (QUAPHS) with Those Derived from (a) Larson-Buswell Equation (LARBPHS), (b) Basic Langelier Equation (LANGPHS) and (c) Caldwell-Lawrence Diagrams (CDLMPHS).

Table 14. Statistical Analysis of the Comparison of the Mean pHs Values Obtained from the Different Calculation Methods

Analysis of Variance				
Source	Degrees of Freedom (df)	Sum of Squares	Mean Square	F calc. ($\alpha = 0.05$)
Model	7	41.788	5.970	28.13 PR>F 0.0001
Error	1088	230.900	0.212	Table F.
Corrected				$F^7 = 2.64$
Total	1095	272.688		1088; 0.05

Duncan's Multiple Range Test*
(Means with the same letter are not significantly different.)

$\alpha = 0.05$		df = 1088	MSE = 0.212
Grouping	Mean	N	Calc. Procedure
A	7.938	137	CDLWPHS
B	7.474	137	STA4PHS
B	7.467	137	STA5PHS
B	7.457	137	QUAPHS
B	7.419	137	WSP2PHS
B	7.414	137	SIMPHS
B	7.357	137	LARBPHS
C	7.211	137	LANGPHS

*df = degrees of freedom; MSE = mean square error; and N = total number of observations or water samples used in the statistical test.

Only the mean values of CDLWPHS and LANGPHS were significantly different from the others. The pH means of the rest were statistically the same.

An additional statistical test was used to compare each QUAPHS value with that derived from the other calculation procedures. The results of the paired comparison analyses are presented in Table 15. As the calculated t values indicate, the differences between each pair of pHs values, that is

each QUAPHS compared to that obtained from each of the seven calculation methods, are all significant. Similarly, the values from the two logarithmic predictive pHs equations are different.

Table 15. Paired Comparison Analysis Between the Individual pHs Value Obtained from the Quadratic Equation and the Value Derived from each of the Rest of the Calculation Methods*

Between	$t_{\text{calc.}}$
QUAPHS and SIMPHS	19.13
QUAPHS and WSP2PHS	11.05
QUAPHS and STA4PHS	5.62
QUAPHS and STA5PHS	8.56
QUAPHS and LANGPHS	47.04
QUAPHS and LARBPHS	12.65
QUAPHS and CDLWPHS†	83.29
STA4PHS and STA5PHS	4.57

* N = 155; t (table): $t_{0.05; 154} = 1.645$.

† N = 137; t (table): $t_{0.05; 136} = 1.645$.

It has been previously noted that the value of QUAPHS was calculated by considering ion pair formation and activity correction factors. To assess how ion pairing and incorporation of activity coefficients would affect the calculation of pHs, the values of SIMPHS and LANGPHS were compared to QUAPHS for two representative water samples. Table 16 lists the important analytical parameters characterizing the two waters.

Table 16. Analytical Parameters Characterizing Water
Samples 22 and 32

Parameter*	Water Number	
	22	32
TDS	390	449
Ca	71	57
Mg	23	31
Na	0	28
SO ₄	102	10
Cl	14	90
Fe	0.2	0.0
F	0.0	2.7
Alk	147	189
Hard	272	269
pH	8.20	7.40
Ionic Strength	0.0092	0.0094
% Free Ca ⁺²	89.6	94.8
% CaHCO ₃ ⁺	3.2	4.3
% CaSO ₄ ⁰	7.1	0.7
% CaCO ₃ ⁰	0.1	0.2
QUAPHS	7.44	7.41
STA5PHS	7.45	7.42
SIMPHS	7.39	7.37
LANGPHS	7.18	7.17
SI†	+0.76	-0.01

* Concentrations are expressed in mg/l from TDS to F and in mg/l as CaCO₃ for Alk and Hard. Ionic strength is in moles/l.

† SI = pH-QUAPHS.

Both waters have comparable hardness and TDS typical of drinking waters. Water number 22 has a QUAPHS of 7.44 with a Ca^{+2} ion pairs constituting 10.4% of the total analytical concentration of calcium. These ion pairs were mainly in the form of CaSO_4° and CaHCO_3^+ . If Ca^{+2} ion pairs were not taken into account, and the total calcium concentration were used, the resulting pHs value would be close, if not equal, to SIMPHS which was derived without considering ion pair formation. The logarithmic value of the total calcium concentration of 71 mg/L is 1.85. If the free Ca concentration were used, the logarithm of $[(0.896)(71)]$ or 63.6 mg/l would be 1.80 which is 0.05 lower. This difference of 0.05 is equal to the difference between QUAPHS and SIMPHS. For water number 32, the logarithm of the total ($\text{Ca}_t = 57$) and free ($\text{Ca}_f = 0.948 \times 57 = 54$) calcium concentrations are 1.76 and 1.73, respectively. The difference of 0.03 is close to the difference of 0.04 between QUAPHS (7.41) and SIMPHS (7.37). Since the observed difference of 0.05 and 0.03 in the two pHs values are within ± 0.05 , the precision of pH measurements, ion pair formation in this particular case would not significantly contribute to the error in the pHs calculation. Errors would start to become critical if the calcium concentration is high enough that ion pair formation amounts to more than 10% of the total Ca^{+2} concentration. Ion pair formation contributing to less than 10% of the complexed Ca^{+2} ion would have an effect of less than 0.05 pHs units for water with 70 to 80 mg/l total calcium concentration.

Using the total analytical concentration instead of activity could yield significant errors in pHs determination. This could be illustrated by comparing SIMPHS with LANGPHS for the above two water samples. The equation for determining SIMPHS contains an activity correction factor while the basic LANGPHS formula does not. A difference of 0.21 between SIMPHS and LANGPHS exists for water 22 and 0.20 for water 32. These differences are significant, especially when dealing with logarithmic values. The activity coefficients of Ca^{+2} ion in waters 22 and 32 are respectively, 0.690 and 0.688. Using the relationship $\text{activity} = \gamma \times \text{concentration}$, and transforming moles/l into mg/l, the Ca^{+2} activity would be 49.0 mg/l for water 22 and 39.2 mg/l for water 32, thus yielding a logarithmic value of 1.69 for the former and 1.59 for the latter. Comparing these values of Ca^{+2} activities with 1.85, the logarithm of total Ca^{+2} concentration of water 22 and with 1.76 of water 32, shows a difference of 0.16 and 0.17 respectively. The difference of 0.03 between 0.20 and 0.17 can be attributed to the correction for the activity of HCO_3^- or CO_3^{2-} which is higher in water 22 due to its higher pH.

One serious drawback in using the LANGPHS equation without considering ion pairing and correcting for activities, is that it gives lower values for the pH of CaCO_3 saturation, thereby giving a higher tendency to obtain

positive saturation indices. For instance, if LANGPHS was used for water 32, the saturation index would be +0.23, meaning that the water had a tendency to deposit CaCO_3 . Using a more accurate pHs value such as QUAPHS or STA5PHS yields a saturation index of -0.01 or -0.02 indicating that the same water would be almost stable with a slight possibility of dissolving a CaCO_3 precipitate. Hence, a plant operator could be led to making a wrong decision when judging the stability of his processed water. Different conclusions about the saturation index of a given water may be drawn if the pHs determination was by LARBPHS method or the Caldwell-Lawrence diagrams. Examination of the values of saturation indices of the 155 water samples reveal that, some waters which have a negative SI using QUAPHS have positive SI when the LARBPHS, and especially the LANGPHS, are utilized in the calculation. Conversely, waters with positive SI evaluated using QUAPHS can have negative SI when the CDLWPHS values are utilized. Thus, it would not be surprising to note that of the 155 water samples, 75 have negative SI when QUAPHS values were used in the determination of saturation indices. Using LANGPHS and LARBPHS values, there would be respectively 38 and 58 waters that would be undersaturated with respect to CaCO_3 , i.e. have negative stability indices. With CDLWPHS, 125 of the waters would exhibit the tendency to dissolve CaCO_3 because their SI values were negative. The observed differences can be understood by examining the activity correction factors used in the pHs calculations. Figure 18 shows how the activity correction factors used in the computation of QUAPHS, SIMPHS, LARBPHS and CDLWPHS vary with ionic strength (I). The equations corresponding to the correction factor are:

Langelier Correction Factor

$$(\text{LANGCF}) = 2.0 (\text{TDS} \times 2.5 \times 10^{-5})^{1/2}$$

Debye-Huckel Correction Factor

$$(\text{DEHLCF}) = \frac{2.5 \sqrt{I} + 3.63 I}{1.0 + 3.3 \sqrt{I} + 2.61 I}$$

Larson-Buswell Correction Factor

$$(\text{LARBCF}) = \frac{2.5 \sqrt{I}}{1.0 + 5.3 \sqrt{I} + 5.51 I}$$

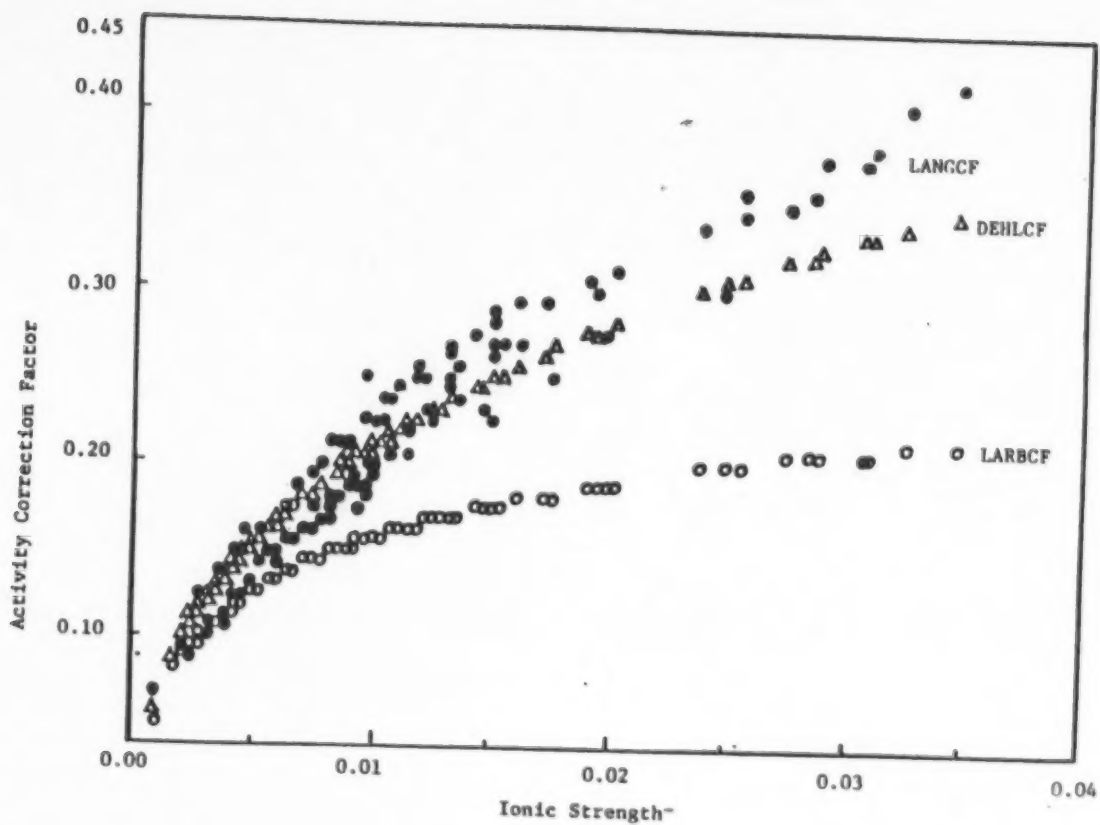


Figure 18. Variation of Activity Correction Factors with Ionic Strength.

As the ionic strength increases, the difference between correction factors likewise increases. The correction factor LANGCF, associated with Langelier's approach, which approximates the ionic strength from the relationship $I = \text{TDS} \times 2.5 \times 10^{-5}$, tends to become larger than the Debye-Huckel factor (DEHLCF) when ionic strength exceeds 0.01 M. This would contribute to higher pHs values as shown by the CDLWPHS values, which are graphically estimated using the Langelier's ionic strength approximation formula. Of course, part of the increase in pHs values derived from Caldwell-Lawrence diagrams could be due to the difficulty in accurately reading the exact intersection point upon which the pHs value is dependent. With higher pHs values, there will always be a greater tendency to obtain a negative saturation index as has been found for CDLWSI. On the other hand, the correction factor developed by Larson and Buswell has a pronounced tendency to be lower than the correction factor derived from the extended Debye-Huckel equation, the difference increasing with increase in ionic strength. Therefore, lower pHs values would be obtained using the Larson-Buswell approach. As a result, 17 waters were found to be undersaturated with respect to CaCO_3 using LARBSI but have positive saturation indices using QUASI.

Based on a comparative analysis and an inspection of the pHs values, the calculation procedure utilizing the STA5PHS formula yields pHs values very close to the exact values obtained by QUAPHS and WSP2PHS, which were determined through an iterative computer calculation involving ionic speciation under equilibrium conditions. The STA5PHS predictive equation is, therefore, recommended for calculation of the pHs of waters with chemical compositions that fall within the range of the analytical parameters characterizing the 155 water samples used here. The computational method utilizing STA5PHS is not only sufficiently accurate, but also is quick and easy to use. The method, in addition, is compatible with the chemical principles behind CaCO_3 solubility equilibrium because the STA5PHS equation is a linear combination of the logarithmic values of TDS, total alkalinity, and total analytical concentrations of calcium, magnesium, and sulfate. TDS is indicative of ions present in the solution. Calcium and alkalinity, to a greater extent, are directly related to the CaCO_3 saturation state, while magnesium and sulfate are involved in ion pairing which, if extensive, could significantly reduce the thermodynamic potential for CaCO_3 deposition.

Experimental Evaluation of the CCO_3 Saturation States of the Water Systems

Whether a given water will dissolve or precipitate CaCO_3 can be determined by equilibrating the water with calcite. De Martini (25) and Hoover (26) had previously described a method in which the water was treated with powdered CaCO_3 and the changes in pH, alkalinity, and calcium

were measured after allowing the solids to settle. This procedure, which was called the marble test, is similar in principle to the method of Enslow (28,29) who developed the continuous stability indicator test wherein the saturation state of the water was determined by equilibrating the flowing water with marble chips for 3 hours. Recently, Merrill and Sanks (18) extended the equilibration time of the marble test to about 12 hours after introducing 0.1 to 0.2 g of finely divided CaCO_3 into a Biochemical Oxygen Demand (BOD) bottle completely filled with water. The difference in calcium concentration between a blank and a calcite-treated solution indicates the precipitation or dissolution potential of the water.

Equilibration experiments similar to marble tests were done to characterize the behavior of the water's pH, alkalinity, and calcium concentration with time after treating the test water with 0.25 ± 0.03 g of Analytical Reagent grade CaCO_3 powder and agitating the water container in a constant temperature water bath set at 25°C . Two water samples were used: Gainesville tap water ($\text{SI} = -0.10$) and deionized water. After various time intervals, the calcium activity was measured using EDTA¹ complexometric titration with the aid of calcium-selective electrode. The pH and total alkalinity were also determined on an aliquot in a sealed container. The results for Gainesville tap water are shown in Figure 19. No significant change in calcium activity was observed in the control. For the CaCO_3 -treated solution, there was a slight change in calcium activity after 3 to 6 hours followed by an increase after 12 to 48 hours. This increase indicates that the water dissolved a small portion of the added CaCO_3 powder such that the pH, and to a slight extent, alkalinity, showed a parallel increase. Figure 20 depicts the changes of calcium concentration, pH, and alkalinity with equilibration in the deionized water. Alkalinity and pH increased almost linearly in the first 24 hours and then exhibited no significant change in the next 24 hours. However, calcium concentration showed a continuous decrease after the first 12 hours and then did not change very much after 36 hours. Since the deionized water contained no CaCO_3 , the tendency of the added calcite powder to dissolve in the first 6 to 12 hours was very strong, indicating that the dissolution process in the CaCO_3 solubility equilibrium was very much favored. Then to maintain equilibrium, some of the dissolved Ca^{+2} reprecipitated. The increase in pH and alkalinity is consistent with the fact that CaCO_3 went into the solution because the dissolving potential of the deionized water is appreciable. As CaCO_3 continuously dissolved, the CO_3^{-2} increased, thus raising the alkalinity even though some of the CO_3^{-2} ions were transformed

¹ EDTA = Ethylenediaminetetraacetic acid.

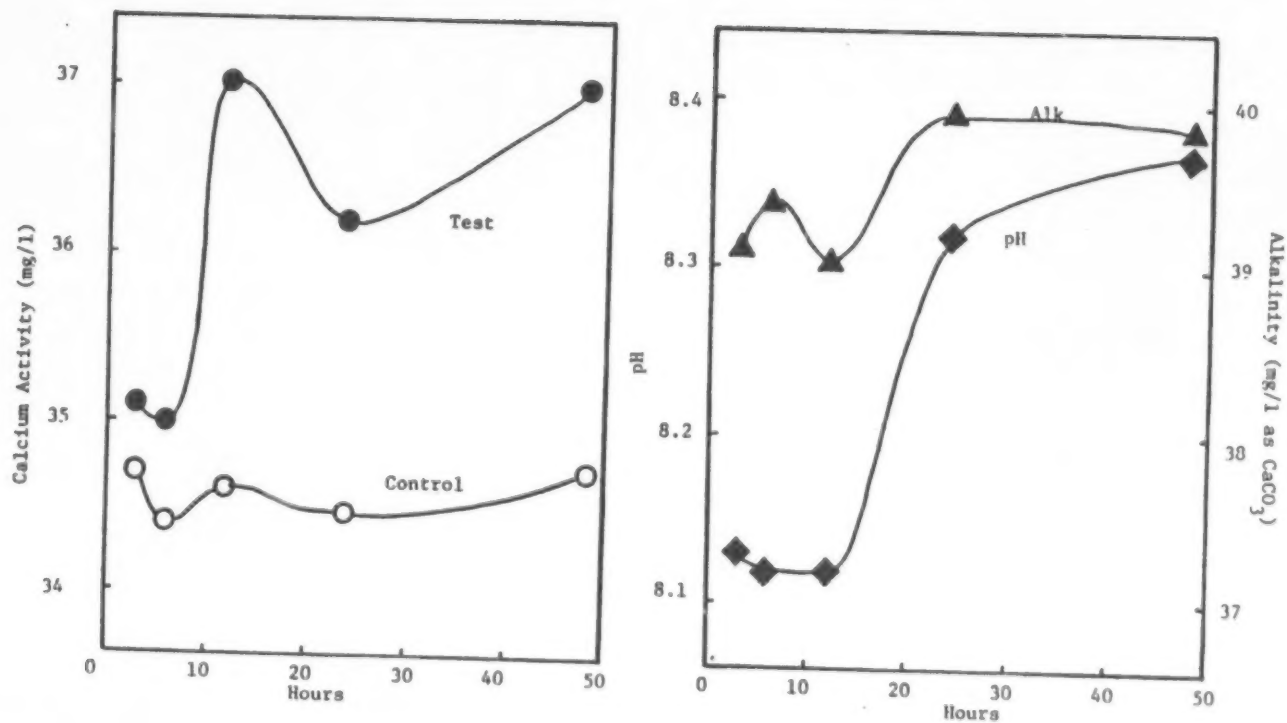


Figure 19. Results of Equilibration Experiments Using Gainesville Tap Water.

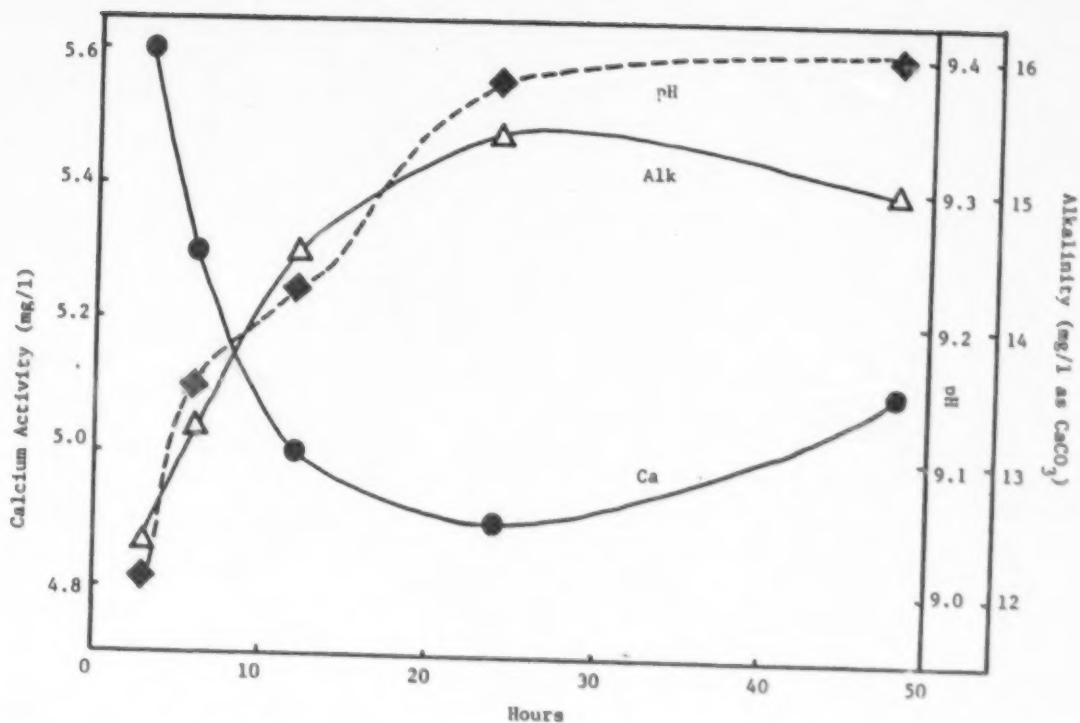


Figure 20. Behavior of Calcium Activity, pH, and Total Alkalinity with Time During the Equilibration Tests Using Deionized Water.

into HCO_3 ions. The final pH after 48 hours was 9.40, which indicates the predominance of carbonate species.

The results of the equilibration experiments suggest that in a water with a slight tendency to dissolve calcium carbonate and in a water with a high dissolving tendency, changes in pH and alkalinity, and especially calcium, are no longer very significant under the conditions of the test after 24 hours. So, 24 hours was the equilibration time chosen in the subsequent evaluation of the saturation state of the water samples. The marble tests described by De Martini (25) and Hoover (26) which required analysis of calcium, pH, and alkalinity right after settling had a very short equilibration periods. The 3-hour equilibration time utilized by Enslow (28,29) in his continuous stability indicator test is also not long enough. Nonetheless, it would be difficult to know the exact equilibration time applicable for all waters of different chemical composition. It is possible that a longer equilibration period is necessary. In some natural waters, attainment of calcite solubility equilibrium has been reported to take 70,000 years (81).

Several synthetic waters with different saturation indices have been evaluated with respect to their CaCO_3 - dissolving or CaCO_3 - precipitating tendency before each water was actually used in the corrosion studies. The compositions of the water used in the jar corrosion tests and those used in the loop studies are presented in Tables 17 and 18 respectively. In the equilibration tests, the total calcium concentration was determined by using Atomic Absorption Spectrophotometry. The results of the experimental determination of the saturation states of the water samples are shown in Table 19. Waters a and b do not contain calcium. Therefore, the definition of saturation index is meaningless for these waters. They, though, exhibited a high dissolving power as evidenced by the changes in pH, alkalinity, and total calcium. Except for water j, all waters with negative saturation index dissolved a certain portion of the added CaCO_3 powder, while those with positive saturation index precipitated calcite. Water j has a saturation index of -0.07 and was, therefore, expected to dissolve CaCO_3 . Instead, a decrease in calcium concentration was observed indicating that no dissolution took place. This unexpected result somehow suggests the limitation or the degree of accuracy to be associated with the prediction of the saturation index formula which only indicates the directional tendency of a water to dissolve or precipitate calcium carbonate. Careful judgment should be exercised in interpreting the possible meanings of the saturation index. Consequently, it would be reasonably safe to put the limit of sensitivity of SI at +0.10.

Table 17. Composition of the Synthetic Water Samples Used in the Jar Test*

Water	TDS	Ca	Mg	Na	Cl	SO ₄	Alk	Hard	pH	pHst	SI
a	4	--	--	--	--	--	2	--	6.00	--	--
b	184	--	24	23	35	96	4	99	6.10	--	--
c	15	4	--	--	--	--	8	10	8.85	9.71	-0.86
d	25	5	--	--	--	--	15	12	9.35	9.37	-0.02
e	116	10	8	27	18	32	21	58	6.95	9.07	-2.12
f	353	34	20	49	60	126	58	167	6.70	8.18	-1.48
g	369	45	2	71	79	80	75	121	6.90	7.96	-1.06
h	537	60	35	56	107	181	80	294	7.10	7.83	-0.73
i	182	20	4	30	35	29	62	66	7.80	8.31	-0.51
j	188	29	13	7	28	38	60	126	8.10	8.17	-0.07
k	791	119	52	55	211	208	120	511	7.45	7.38	+0.07
l	210	27	4	33	46	25	77	81	8.25	8.12	+0.13
m	586	98	4	80	173	16	176	261	7.80	7.26	+0.54
n	698	84	40	73	149	159	159	375	8.25	7.39	+0.86
o	528	75	12	71	133	47	156	237	8.45	7.42	+1.03
p	680	100	18	88	178	84	174	324	8.70	7.27	+1.43
q	679	120	5	130	213	20	232	321	8.95	7.05	+1.90

* All water samples were synthetically prepared except water a, which is deionized water.

† Computed using the five-variable logarithmic model for pHs (STA5PHS).

Table 18. Composition of the Synthetic Water Samples Used in the Loop Studies

Water	TDS	Ca	Mg	Na	Cl	SO ₄	Alk	Hard	pH	pHs*	SI
A	193	26	4	28	46	16	60	81	7.50	8.22	-0.72
B	446	40	17	68	71	69	148	170	7.25	7.71	-0.46
C	175	19	5	27	36	22	54	68	7.85	8.40	-0.35
D	312	15	15	55	27	85	94	99	8.35	8.31	+0.04
E	550	120	13	42	213	51	91	353	8.00	7.43	+0.57
F	633	78	30	75	137	119	159	319	8.35	7.41	+0.94

*Computed from STA5PHS equation.

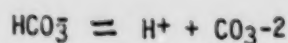
Table 19. Results of the Experimental Evaluation of the Saturation States of the Water Samples Used in the Jar Corrosion Tests (a-q) and Loop Studies (A-F)

Water	SI	pH		Alk (mg/l as CaCO ₃)		Ca (mg/l)	
		Initial	Final	Initial	Final	Initial	Final
a	--	6.00	9.40	2	15	0	6.0
b	--	6.10	9.25	4	16	0	6.5
c	-0.86	8.85	9.35	8	15	4	5.5
d	-0.02	9.35	--	15	--	5	--
e	-2.12	6.95	8.25	21	26	10	15.5
f	-1.48	6.70	7.75	58	72	34	39.0
g	-1.06	6.90	7.60	75	85	45	50.0
h	-0.73	7.10	7.30	80	86	60	65.0
i	-0.51	7.80	7.90	62	65	20	24.0
j	-0.07	8.10	7.90	60	56	29	26.0
k	+0.07	7.45	7.30	120	95	119	107.0
l	+0.13	8.25	7.85	77	70	27	25.0
m	+0.54	7.80	7.40	176	151	98	77.0
n	+0.86	8.25	7.75	159	134	84	74.0
o	+1.03	8.45	7.55	156	118	75	60.0
p	+1.43	8.70	7.70	174	155	100	92.0
q	+1.90	8.95	7.05	192	135	120	94.0
A	-0.72	7.50	7.60	60	64	26	28.0
B	-0.46	7.25	7.55	148	167	40	46.0
C	-0.35	7.85	7.90	54	57	19	21.0
D	+0.04	8.35	8.10	94	93	15	17.0
E	+0.57	8.00	7.50	91	78	120	114.0
F	+0.94	8.35	7.65	159	136	78	66.0

This means that if the saturation index is between ± 0.10 , it would be difficult to decide with confidence the actual saturation state of the water.

Relationship of Saturation Index to the Gibbs Free Energy Change

Since the saturation index is an indication of the tendency of the water to precipitate or dissolve calcium carbonate, it can be related to the driving force of the calcite solubility equilibrium. From the dissociation of the bicarbonate ion



$$K_2 = \frac{\{\text{H}^+\} \{\text{CO}_3^{2-}\}}{\{\text{HCO}_3^-\}}$$

$$\text{or } \{\text{H}^+\} = \frac{K_2 \{\text{HCO}_3^-\}}{\{\text{CO}_3^{2-}\}} \quad (30)$$

in which $-\log \{\text{H}^+\}$ can be equated to the actual pH of the water.

It has been shown that for acid dissolution of calcite

$\text{CaCO}_3(\text{s}) + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^-$
the hydrogen ion concentration at CaCO_3 saturation could be expressed as

$$[\text{H}^+] = \frac{K_2'}{K_s} [\text{Ca}^{2+}] [\text{HCO}_3^-]$$

or in terms of activities as

$$\{\text{H}^+\} = \frac{K_2}{K_s} \{\text{Ca}^{2+}\} \{\text{HCO}_3^-\} \quad (31)$$

The calcium carbonate saturation index (SI) is defined as

$$SI = pH - pH_s$$

$$\text{or} \quad SI = \log \frac{\{H_s^+\}}{\{H^+\}} \quad (32)$$

where $\{H^+\}$ is the hydrogen ion activity of the water.

Substituting equation (30) and equation (31) for $\{H^+\}$ and $\{H_s^+\}$

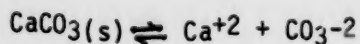
respectively, into equation (32), the expression for saturation index becomes

$$SI = \log \frac{(K_2/K_s) \{Ca^{+2}\} \{HCO_3^-\}}{K_2 (\{HCO_3^-\} / \{CO_3^{2-}\})}$$

which simplifies to

$$SI = \log \left(\frac{\{Ca^{+2}\} \{CO_3^{2-}\}}{K_s} \right) \quad (33)$$

The available free energy under any condition for the solubility of calcite



can be expressed as

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (34)$$

where ΔG = Gibbs free energy for the reaction,

ΔG° = standard free energy change,

R = universal gas constant,

T = temperature ($^\circ K$), and

Q = reaction quotient which is similar to an equilibrium constant.

At equilibrium, $\Delta G = 0$, and the reaction quotient Q becomes the equilibrium

constant, that is $Q \rightarrow K_s$.

Therefore,

$$\begin{aligned} 0 &= G^\circ + RT \ln K_s, \text{ or} \\ \Delta G^\circ &= - RT \ln K_s \end{aligned} \quad (35)$$

Using equation (35) in equation (34), the Gibbs free energy change becomes

$$\begin{aligned} \Delta G &= RT \ln K_s + RT \ln Q \\ &= RT \ln \frac{Q}{K_s} \end{aligned} \quad (36)$$

which, for the calcite solubility reaction,

$$\begin{aligned} Q &= \{Ca^{+2}\} \{CO_3^{-2}\} \\ K_s &= \{Ca^{+2}\}_e \{CO_3^{-2}\}_e \end{aligned}$$

with the subscript e indicating equilibrium conditions. Utilizing $\ln x = 2.303 \log x$, equation (36) can be rewritten (in terms of logarithm to the base 10) as

$$\Delta G = 2.303 RT \log \left(\frac{\{Ca^{+2}\} \{CO_3^{-2}\}}{K_s} \right) \quad (37)$$

Substituting equation (33) into equation (37) yields

$$\Delta G = 2.303 RT (SI) = 10364 (SI) \text{ kcal mole}^{-1} (25^\circ\text{C}) \quad (38)$$

which relates the saturation index to the Gibbs free energy change involved in calcite precipitation or dissolution. When the saturation index is

positive, ΔG is also positive which means the reaction as written, that a CaCO_3 dissolution, is not spontaneous. This is tantamount to saying that the backward reaction, CaCO_3 precipitation, is thermodynamically favored. This is consistent with the meaning associated with positive SI, which indicates that the water has a tendency to deposit CaCO_3 . On the other hand, a negative SI will yield a negative ΔG which denotes that the forward reaction or calcite dissolution is spontaneous. Again, this agrees with the scale-dissolving tendency of a water with a negative SI. When SI is equal to zero we have an equilibrium condition which corresponds to $\Delta G = 0$.

Equation (38) was used in determining the free energy change for the spontaneity or nonspontaneity of calcium carbonate dissolution in the waters used for corrosion studies. The results of the ΔG calculation are shown in Table 20. It should be noted that the waters with higher positive values of the saturation index also have larger free energy changes indicating the stronger tendency to form CaCO_3 coatings. However, ΔG , being a thermodynamic parameter, cannot furnish information as to the rate of deposition of calcium carbonate.

The mathematical relationship between the saturation index and the Gibbs free energy charge derived in this study differs slightly from the equation reported by Trussell (82) in 1978 which defined ΔG in terms of SI as

$$\Delta G = \frac{2.3}{RT} \ln \frac{Q}{K_s}$$

Corrosion Studies in Jar Systems

MILD Steel

Several synthetic waters with different saturation indices were used in the jar corrosion tests. In addition, waters with different calcium concentrations, total alkalinities, and pH levels were evaluated for their corrosive characteristics in the jar systems.

Corrosive Behavior of the Waters with Various Saturation Indices toward Mild Steel

Fifteen synthetic waters with different saturation indices were used in the jar corrosion experiments. In addition, two more water samples were utilized to compare their corrosion characteristics with the waters containing calcium and alkalinity. The first water, labeled a in Table 17, was deionized water, and second, b, was deionized water spiked with 1.0 millimole of NaCl and 1.0 millimole of MgSO_4 . The third water, c, was

Table 20. Change in Gibbs Free Energy Value at 25°C Associated with the Tendency of the Water to Dissolve or Precipitate Calcium Carbonate

Water	Saturation Index	ΔG (kcal mole ⁻¹)
a	—	—
b	—	—
c	-0.86	-1.173
d	-0.02	-0.027
e	-2.12	-2.892
f	-1.48	-2.019
g	-1.06	-1.446
h	-0.73	-0.996
i	-0.51	-0.696
j	-0.07	-0.095
k	+0.07	+0.095
l	+0.13	+0.177
m	+0.54	+0.737
n	+0.86	+1.173
o	+1.03	+1.405
p	+1.43	+1.951
q	+1.90	+2.592
A	-0.72	-0.982
B	-0.46	-0.627
C	-0.35	-0.477
D	+0.04	+0.055
E	+0.57	+0.777
F	+0.94	+1.282

deionized water treated with enough calcite powder to make it unsaturated with respect to CaCO_3 . About 17 grams of calcite powder was equilibrated in 21 liters of deionized water for 24 hours and the resulting supernatant was used as the CaCO_3 saturated water labeled as d. The saturation index of the remaining waters e to q was adjusted with the aid of STA5PHS formula by adding appropriate quantities of the required reagents. The corrosion rate of mild steel coupons immersed in each water after 1, 3, 5, and 10 days were measured by the weight-loss method. Figure 21 shows the variation of corrosion rate with time in jar systems containing 5 ± 0.2 mg/l dissolved oxygen. The corrosion rate of mild steel in all the waters tested exhibited a general decreasing trend with time. Corrosion was very rapid in the first- and third-day immersion period and then did not change much between the fifth and tenth day. The decreasing corrosion rate trend could be attributed to two important factors. The first is the formation of corrosion products that adhered to the metal surface and decrease the progress of corrosion either by passivating the metal or by providing a protective coating on the metal surface against further corrosive attacks.

The second could be the decrease of the thermodynamic potential of the metal to further release metallic ions into the solution after the water became enriched with those ions during the initial stages of corrosion. Of course, this depends on the assumption that the oxidation of ferrous to ferric ions and the subsequent formation of iron oxides was not as fast as the release of metallic ions from the metal surface.

The initial corrosion rates of mild steel in deionized water with and without NaCl and MgSO_4 (waters a and b) were higher than for waters treated with CaCO_3 powder (waters c and d) which denotes that carbonate-bearing waters are less corrosive than waters with chloride and sulfate salts. With an increase in alkalinity and calcium concentration, the corrosion rates of mild steel tended to become lower. Hence, waters with negative saturation indices showed faster corrosion rates compared than those with positive saturation indices. The amount of dissolved iron present in each solution at the indicated time interval for the 17 waters is presented in Figure 22. The trend of concentration changes with time varied for each water. For water a (deionized water) and water d dissolved iron increased almost linearly with time, but waters b and c exhibited rapid iron concentration increase during the first three days and then started to decrease. Water j, with a saturation index of -0.07, also showed a continuous increase in dissolved iron. The rest of the waters have more or less comparable concentration change with time patterns in which dissolved iron increase initially and then began to decrease gradually.

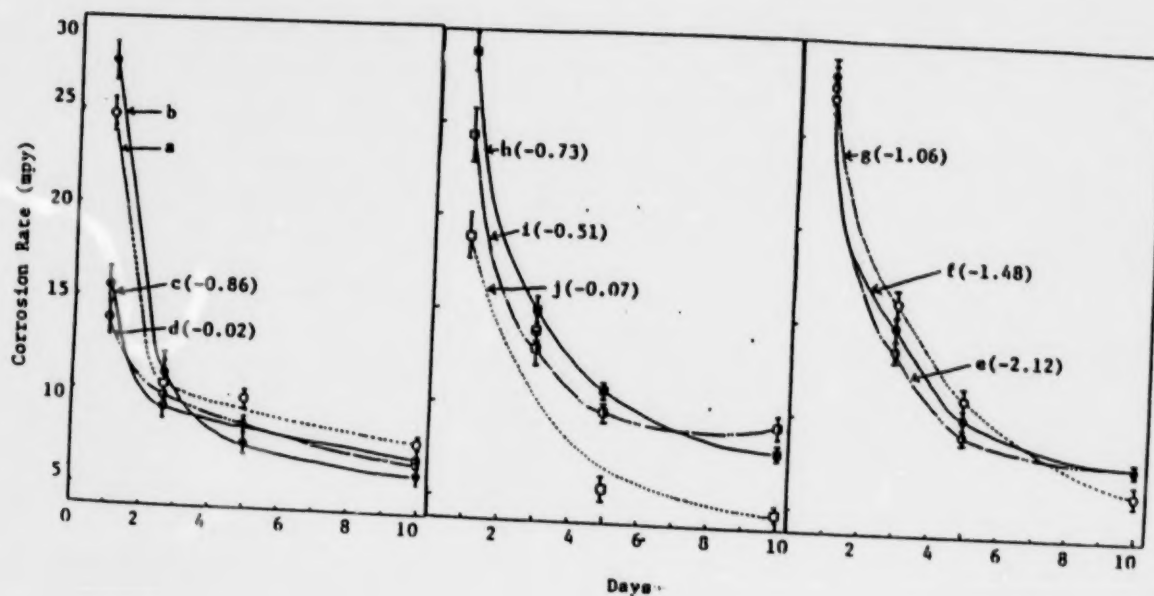


Figure 21. Corrosion Rate-Time Curves for Mild Steel in Synthetically Prepared Waters of Different Saturation Indices. The Saturation Index of Each Letter-Coded Water is Indicated Inside the Parenthesis. Each Vertical Bar Indicated Standard Deviation for 4 Measurements. Dissolved Oxygen was 5.0 ± 0.2 mg/l.

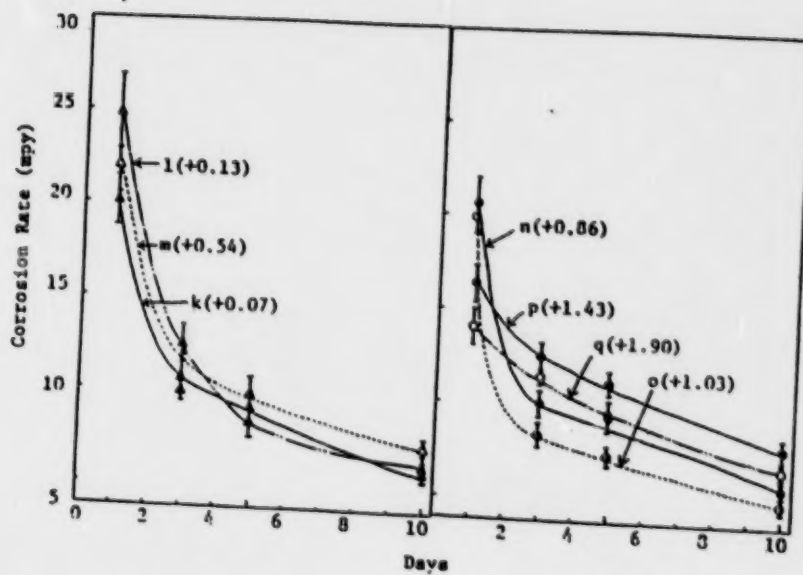


Figure 21. Continued

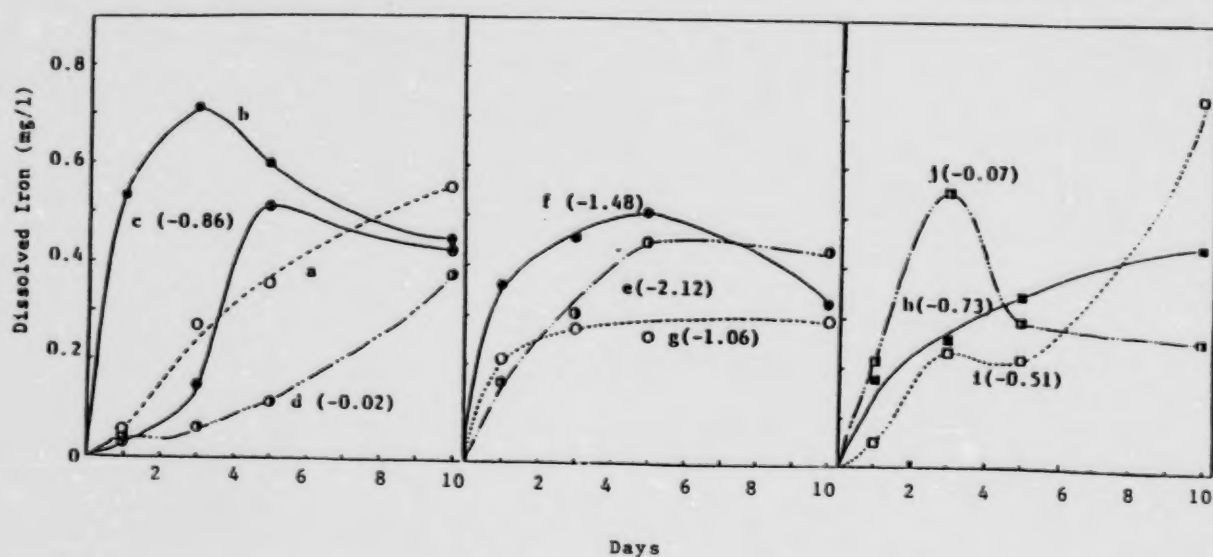


Figure 22. Dissolved Iron Concentration - Time Profiles for the 17 Waters in Contact with the Mild Steel Coupons in the Jar Corrosion Experiments. Dissolved Oxygen in each Experimental Run 5.0 ± 0.2 mg/l. Number Inside the Parenthesis after Each Letter Designating the Water is the Saturation Index.

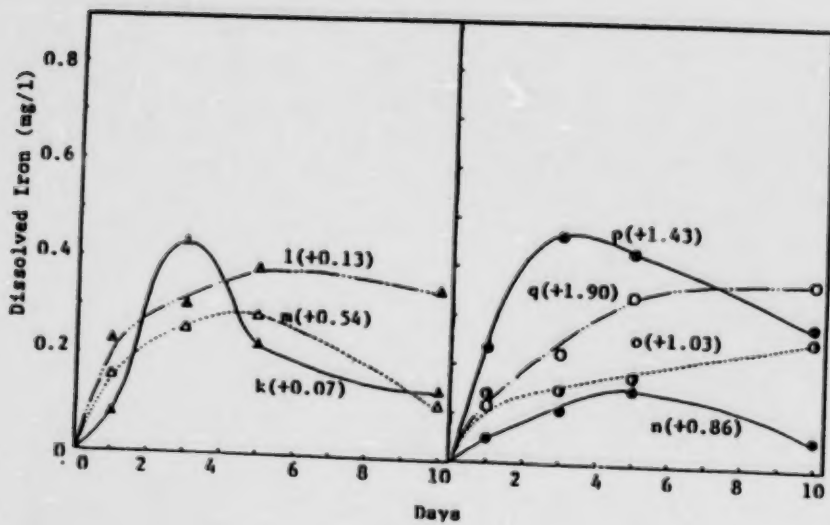


Figure 22. Continued

The decrease in dissolved iron could be due to the declining corrosion rate and the oxygenation of dissolved ferrous and ferric ions to form iron oxides. The average 10-day corrosion rates and average 10-day dissolved iron from the jar tests were computed. The results are summarized in the bar graph shown in Figure 23. Again, except for waters c and d which were respectively under and nearly saturated with CaCO_3 , the average 10-day corrosion rates were generally higher in waters with negative saturation indices. Nevertheless, a decrease in SI did not correlate well with an increasing corrosion rate. For example water g, with $\text{SI} = -1.06$, has a higher average corrosion rate than waters e and f with $\text{SI} = -2.12$ and -1.48 , respectively. Similar anomalies were also found for waters with positive SI. An increase in the positive values of SI did not correspond to decreasing corrosion rates. Water q ($\text{SI} = +1.90$), and especially water p ($\text{SI} = +1.43$), had higher corrosion rates than water o ($\text{SI} = +1.03$). It was also noted that there was not a linear relationship between corrosion rate and dissolved iron, which suggests that associating higher dissolved iron with faster corrosion rate would be misleading. Of course, there are instances when the concentration of dissolved ferrous and ferric ions are high as a result of the continuous rapid leaching of metal ions due to corrosion. But in other situations, the precipitation of dissolved metal ions is more thermodynamically favored in solutions with sufficiently high concentrations of carbonate species and dissolved oxygen such that the precipitation of carbonate salts and oxides of iron could readily occur. Irrespective of the sign and value of the saturation index, any water will be corrosive to a metal in direct contact with that water. Therefore, it is illogical to apply the meanings of the saturation indices as commonly utilized in the water works industry. Stating that a water with a negative SI is corrosive, while a water with a positive SI is non-corrosive, is erroneous. The results of the present study on corrosion experiments indicate that regardless of the algebraic values of the saturation indices, waters with dissolved electrolytes are all corrosive. Hence, the derivation and limitations of the Langelier Index or Saturation Index must be understood in order to make it useful in corrosion control practice.

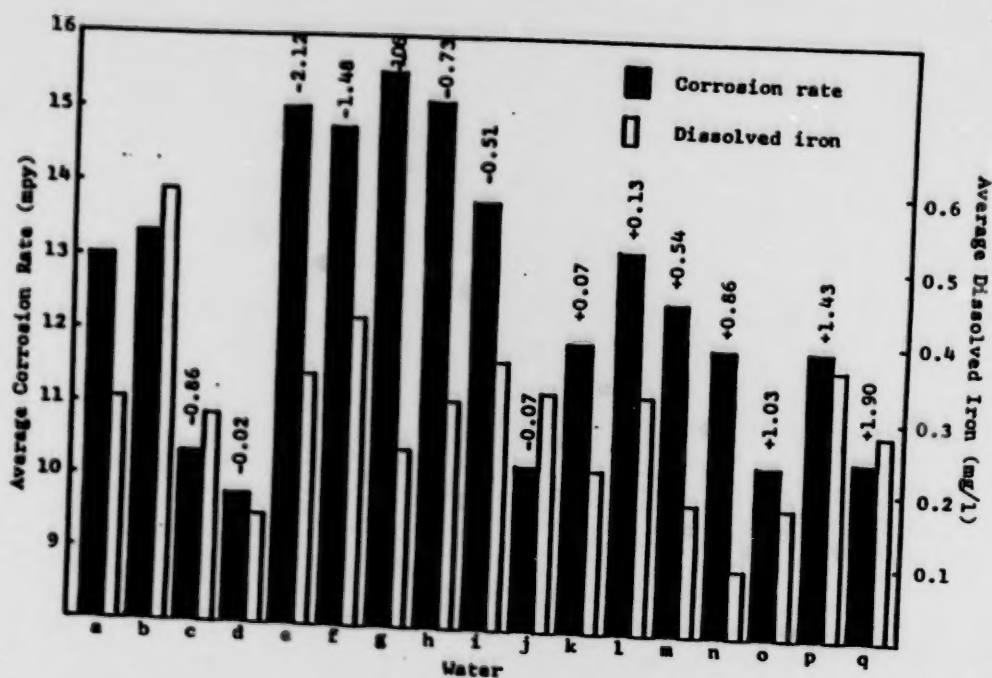


Figure 23. Bar Graph of the Average Corrosion Rate of Mild Steel and Average Total Dissolved Iron of the 17 Test Waters. Numbers above the Corrosion Rate Bars Refer to the Saturation Indices.

Effect of Calcium Concentration

Gainesville tap water and deionized water were used in evaluating the effect of the calcium concentration on the corrosion of mild steel. The analytical parameters characterizing the Gainesville water used are

TDS = 190 mg/l	Alk = 56 mg/l as CaCO_3
Ca = 30 mg/l	Hard = 112 mg/l as CaCO_3
Mg = 14 mg/l	pH = 8.05
Na = 7 mg/l	pHs = 8.17
SO_4 = 34 mg/l	SI = -0.12
Cl = 28 mg/l	

The deionized water was treated with NaHCO_3 to produce an alkalinity of 80 mg/l as CaCO_3 while the calcium level was varied from 0 to 120 mg/l. In Gainesville water, the calcium concentration was varied from its original concentration of 30 mg/l to 160 mg/l. Figure 24 shows the results of the corrosion tests. For both waters, an increase in calcium concentration led to inhibition of corrosion. The reduction of the corrosion rate was more pronounced in the 2-day immersion period than in the longer exposure periods of 5 and 10 days. In the presence of more Ca^{2+} ions, the thermodynamic potential of CaCO_3 precipitation is higher, thus favoring deposition of a calcite protective coating on the metal surface. Larson and Skold (83) observed similar corrosive behavior of machined cast iron specimens in waters containing increasing calcium quantities from 12.5 to 125 mg/l as CaCO_3 . They expressed the broad generalization that irrespective of the saturation index and minor variation in the amounts of chloride and alkalinity, the concentration of calcium is a primary factor in the inhibition of corrosion of cast iron and steel (84).

While the corrosion behavior of mild steel in the two waters is comparable for the first two days, corrosion rates in the Gainesville water after 5 and 10 days were higher than those in the deionized water. This could have been due to higher ionic strengths and, therefore, increasing conductivities of the Gainesville water system which favored a more rapid corrosion rate of mild steel. The effect of conductivity appears to override the possible inhibitive effect of alkalinity, which was slightly lower in the deionized water than in the Gainesville water.

The change in concentration of dissolved iron with time in each water

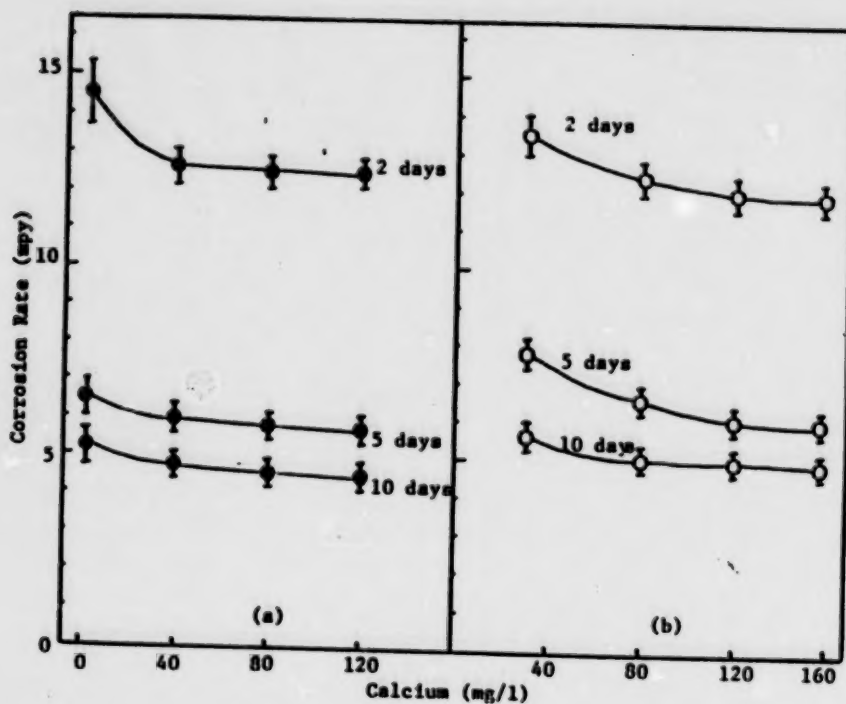
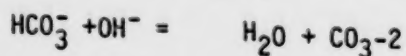
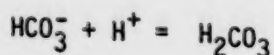


Figure 24. Corrosion Rate of Mild Steel as a Function of Ca Concentration for (a) Treated Deionized Water and (b) Gainesville Water. Dissolved Oxygen was 5.0 ± 0.2 mg/l. The Standard Deviation of 3 Measurements is Indicated by the Bar.

is shown in Figure 25. Except for a sample of Gainesville water with a calcium concentration of 30 mg/l, the trend of dissolved iron changes was similar for both waters. There was a consistent increase in dissolved iron in the first two days followed by a decrease on the fifth and again on the tenth day. The concentrations of iron in the Gainesville water were higher than those in comparable samples of the deionized waters.

Influence of Alkalinity, pH, and Buffer Capacity on the Corrosion of Mild Steel

One important water quality parameter that affects the CaCO_3 dissolving or precipitating tendency is alkalinity. The level of alkalinity at a given pH determines how much carbonate is present and thus available for CaCO_3 deposition. However, alkalinity may not only affect the CaCO_3 solubility equilibrium, but may directly influence corrosion. The alkalinity of the deionized and Gainesville tap waters was varied from 0 to 150 mg/l as CaCO_3 in the former and from 56 to 200 mg/l as CaCO_3 in the latter. Corrosion rates were measured and the results are presented in Figure 26. As with the calcium concentration, increasing levels of alkalinity decreased the corrosion rates, especially after the first two days of immersion in both waters. Again, the corrosion of mild steel in Gainesville water was generally faster than in deionized water for all time intervals. The inhibiting effect of the increase in alkalinity was due to the stronger capacity of the system to prevent significant localized pH changes in the metal surface as corrosion progressed. With increasing concentration of HCO_3^- , any increase in pH in the cathodic zones and decrease in pH in the anodic regions could be counteracted in the presence of bicarbonate ions according to the following ionic equilibrium reactions:



The solution in the immediate vicinity of the anodic areas could be prevented from becoming too acidic by the formation of carbonic acid which is a weak acid. On the other hand, increasing basicity in the cathode solution could be offset by the hydroxylation of the bicarbonate ion. When the pH difference between the cathode and anode regions decreases, the driving force of the redox processes would be reduced, thus slowing down the corrosion rate. Hatch and Rice (85) studied the influence of alkalinity on the corrosion of steel in the presence of chloride and sulfate salts. Substantial reduction of corrosion rates were observed as the alkalinity of the solution was raised from 25 to 50, then to 100 mg/l as CaCO_3 . Larson and Skold (84) concluded from their

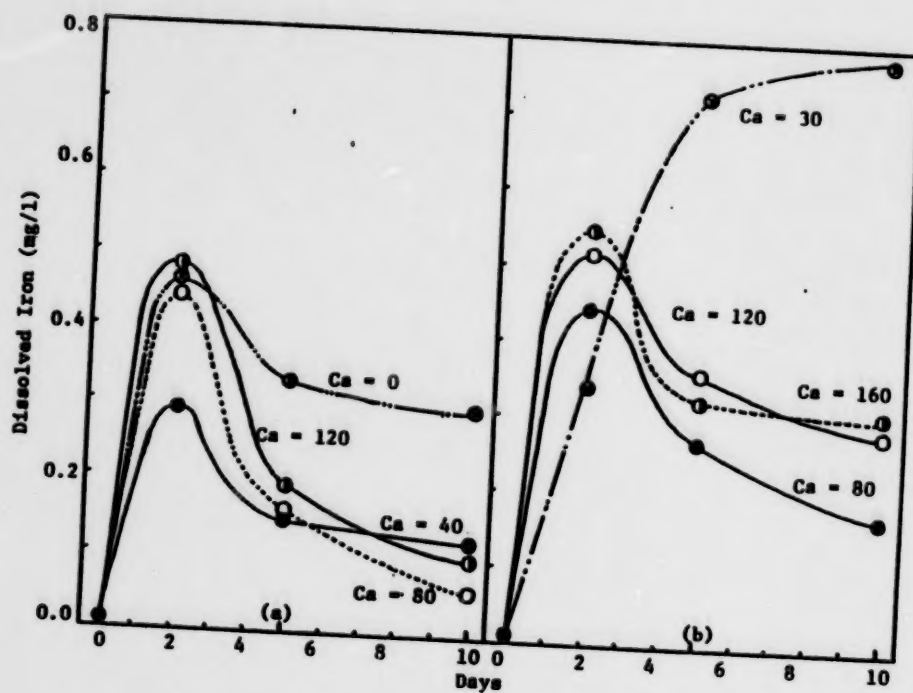


Figure 25. Total Dissolved Iron Concentration - Time Profile for (a) Treated Deionized Water and (b) Gainesville Water.

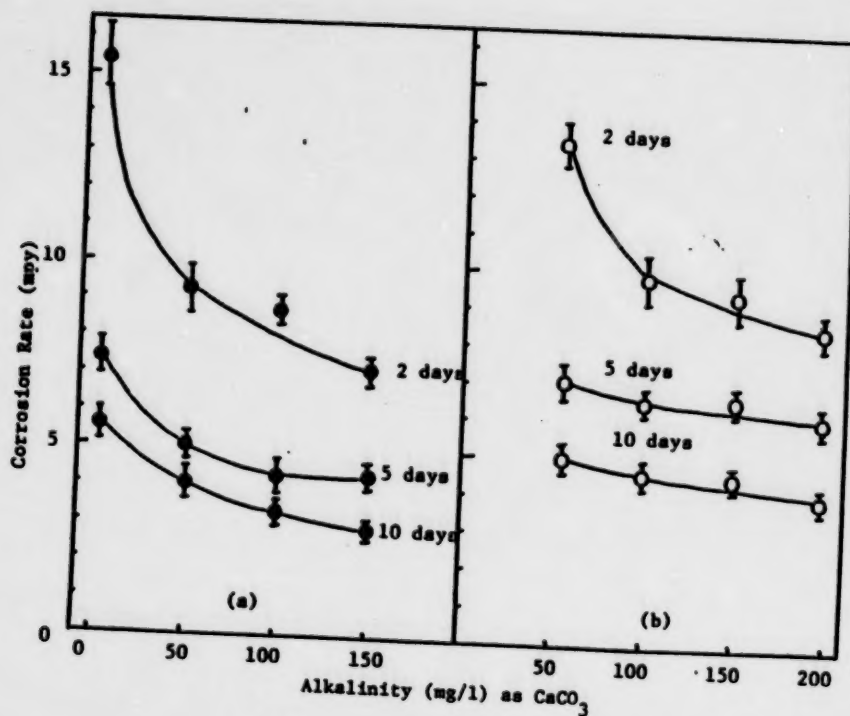


Figure 26. Variation of Corrosion Rate of Mild Steel with Alkalinity at Different Exposure Times for (a) Treated Deionized Water and (b) Gainesville Water. Ca Concentration in (a) and (b) Is Respectively 40 and 30 mg/l. The Bar Shows Standard Deviation for 3 Measurements.

laboratory studies of the corrosion of steel and cast iron that alkalinity, or HCO_3^- , was an inhibitive agent against corrosion.

The variation of dissolved iron with time in the two test waters was different. As shown in Figure 27 dissolved iron in the deionized water increased after the first two days in the solution containing 100 and 150 mg/l as CaCO_3 and then started to fall off after 5 to 10 days. There was a continuous increase in dissolved iron in the deionized water containing 50 mg/l of alkalinity as CaCO_3 which was similar to the concentration-time trend in Gainesville water with an alkalinity of 56 mg/l as CaCO_3 . The rest of the solutions in Gainesville water with alkalinities of 100, 150, and 200 mg/l as CaCO_3 showed an initial increase after 2 and 5 days followed by a decrease in iron concentration after 10 days. In both waters, dissolved iron decreased with an increase in alkalinity, probably due to the formation of the carbonate salts of iron. The tendency to form siderite (FeCO_3) would be stronger when the water systems contain sufficient quantities of CO_3^{2-} due to high alkalinity content, as has been found in water treatment plants (86). Consequently, some of the iron could be precipitated. This would decrease the concentration of the dissolved iron.

Studies of the effect of pH on corrosion in waters with various concentrations of carbonate alkalinity, were also done by immersing mild steel coupons in jars containing deionized and Gainesville tap water. The water in each jar was previously titrated with either 0.01 N HCl or 0.02 N NaOH to adjust the pH to the desired value. After 3 days, the corrosion rates were determined and the amount of dissolved iron was measured colorimetrically. The results are shown in Figure 27. In both water systems, relatively rapid corrosion rates were found over the acidic pH range of 5.0 to 6.5, while the lowest rate occurred at pH 9.5. Within the limit of the experimental error, no significant difference in corrosion rates was observed over the range pH 7.0 to pH 8.5. At all the pH values considered, corrosion in deionized water proceeded faster than that in Gainesville tap water. The lower corrosion rates in Gainesville water could be due to its alkalinity, which had been found previously to be inhibitive to corrosion.

The results of the present study on the effect of pH on corrosion were slightly different from that reported by other workers. Uhlig (7) presented data indicating that corrosion of iron is independent of pH over the pH range 4.0 to 10.0. Similarly, it has been reported that the corrosion of mild steel in the absence of protective coatings is essentially constant over the range of pH 4.0 to 10.0 at 22°C (87,88). This constancy of corrosion rate over the given pH range could occur in

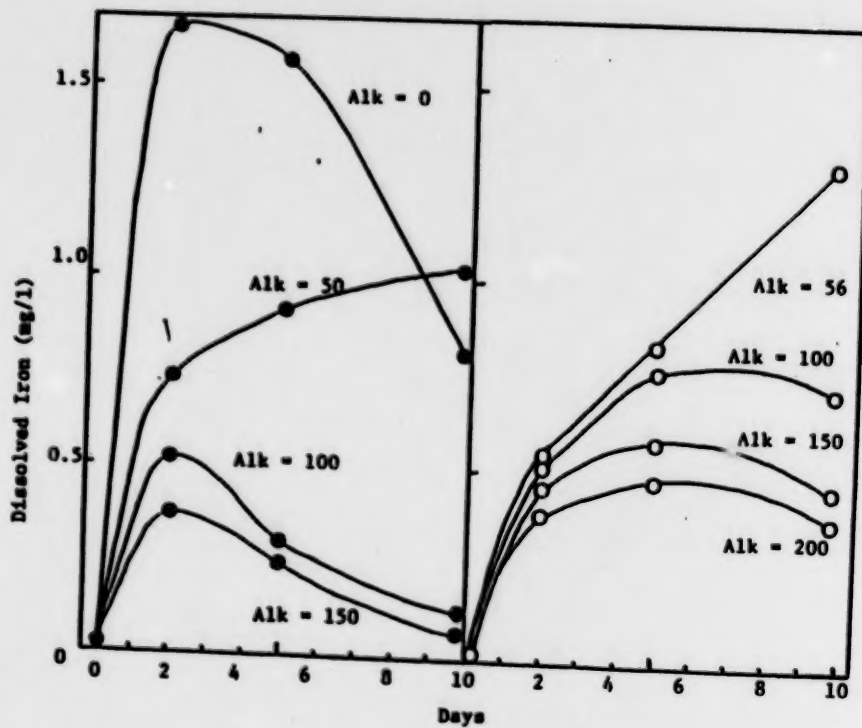


Figure 27. Changes of Total Iron with Time For (a) Treated Deionized Water and (b) Gainesville Water.

solutions that are continuously aerated such that any dependence of corrosion rate on solution factors, such as pH, would be obscured. In this study, the dissolved oxygen in the waters tested was 5.0±0.02 mg/l which may not be high enough to mask the effect of pH, especially in the more acidic region.

As shown in Figure 28, the amount of dissolved iron in Gainesville water at all pH values was higher than that in the deionized water. The difference in iron concentration could have been due to the higher ionic strength of the Gainesville water. As the ionic strength increases, the activity coefficient of an ion decreases, therefore to maintain a certain effective concentration and satisfy its ionic solubility equilibrium, the analytical concentration must increase. The results of the corrosion experiments for evaluating the effect of pH at constant alkalinity are shown in Figure 29. The pH of the solution was adjusted by simultaneously bubbling CO₂ and air through the solution. The buffer capacity (β) was computed at each given pH using an expression of buffer capacity derived as a function of measurable concentrations and known constants.

$$\beta = 2.303 \left\{ \frac{\alpha_2 [\text{H}^+] ([\text{Alk}] [\text{H}^+] + [\text{H}^+]^2 - K_w)}{K_1 [\text{H}^+] + 2K_1 K_2} \left(\frac{[\text{H}^+]}{K_2} + \frac{K_1}{[\text{H}^+]} + 4 \right) + [\text{OH}^-] + [\text{H}^+] \right\}$$

It should be noted that β is a function of α_2 which is directly related to the carbonate ion concentration and in turn could be related to the CaCO₃ solubility product constant and saturation index. If the pH is varied at constant alkalinity or constant total carbonate concentration (C_T), the buffer capacity (or buffer index) of the aqueous solution changes. Figure 30 shows the change in buffer capacity in a solution with 1x10⁻³ moles/l total carbonate concentration from about pH 3.5 to pH 12.0. Maximum buffer capacity is exerted at pH 6.3, which corresponds to pK₁ of carbonic acid. Minimum buffer capacities are found at pH 4.5 and pH 8.3, the latter value being equal to 1/2 (pK₁ + pK₂).

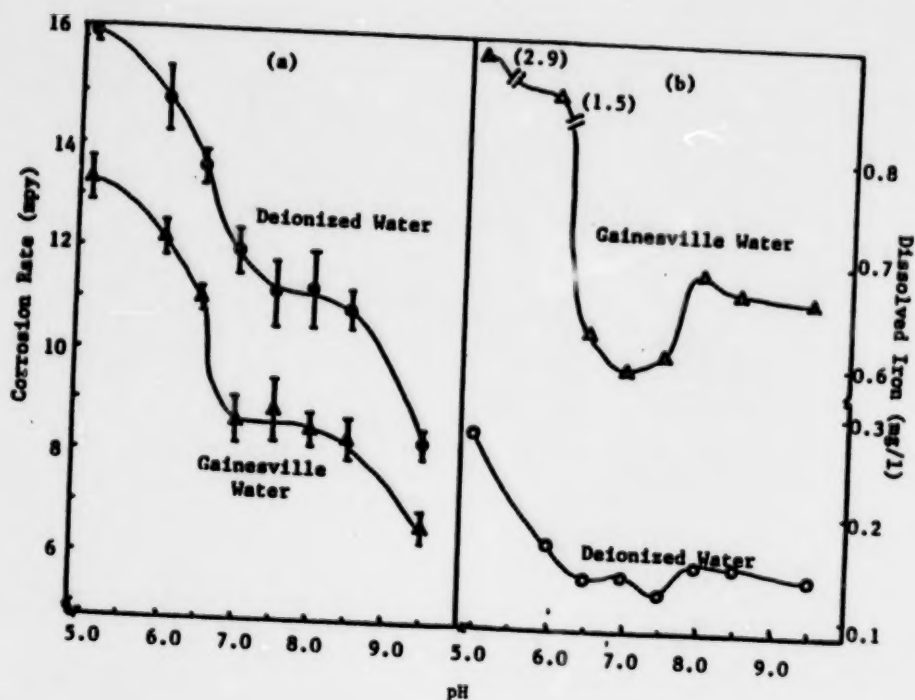


Figure 28. Variation of Corrosion Rate (a) and Dissolved Iron (b) with pH. Dissolved Oxygen in Each Water System was 5.0 ± 0.2 mg/l. Each Data Point Represents the Mean Value of Four Corrosion Rates of Mild Steel After Three Days. Each Bar Indicates Standard Deviation.

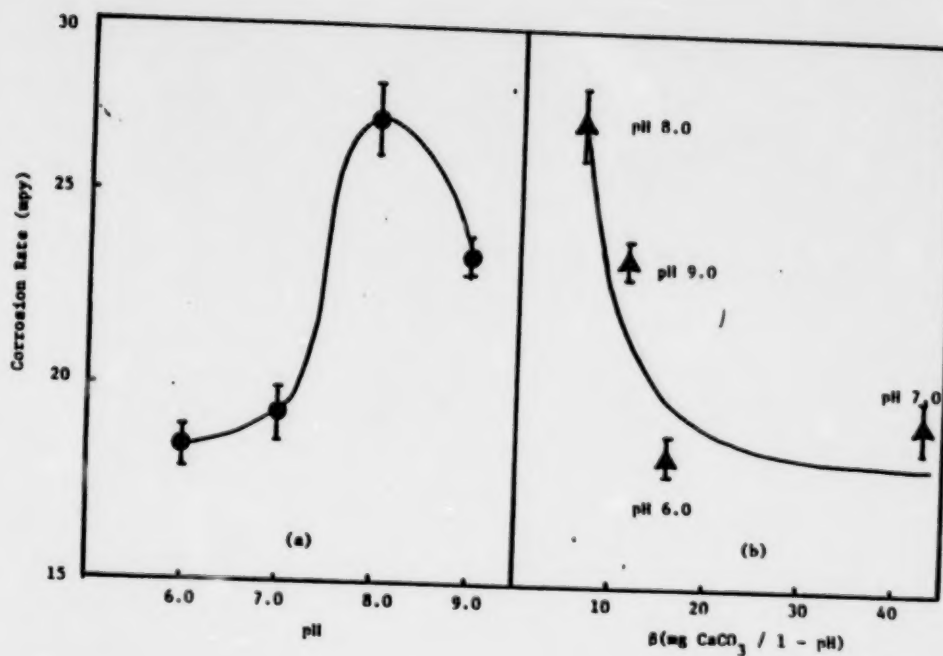


Figure 29. Corrosion Rate of Mild Steel as a Function of (a) pH (b) Buffer Capacity. All Test Waters Contained 100 mg/l as CaCO_3 Alkalinity. Corrosion Rate was Measured after 3 days and the Bar Indicates Standard Deviation.

Figure 29 shows that the corrosion rate of mild steel decreased as the buffer capacity of the solution increased. The highest corrosion rate was at pH 8.0 where the buffer capacity was at a minimum. In corrosion experiments using cast iron in aerated flow cells, Stumm (89) observed that corrosion rates were higher at pH 8.0 to 8.5 and attributed the results to the low buffer capacity in this pH range. Higher corrosion rates of mild steel and cast iron were also found by other investigators (83,84) in waters at pH 8.0 compared to those at other pH values.

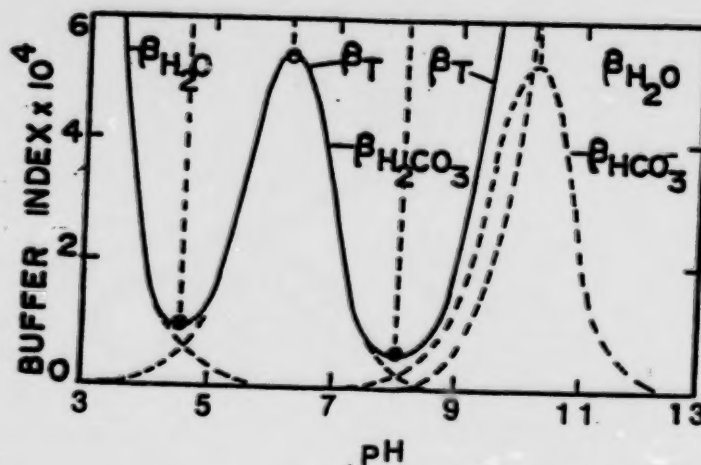


Figure 30. Variation of Buffer Capacity with pH in an Aqueous Solution Containing 1×10^{-3} M of Total Carbonate Species. (Adapted from Reference 52.)

Additional experiments were conducted to determine the effect of buffer capacity on the corrosion of mild steel in waters with different alkalinities and at different pH values. The results are summarized in Table 21. As alkalinity was increased at each pH, the buffer capacity likewise increased. However, this time, the corrosion rates were higher in waters with higher buffer capacities and alkalinities for each value of pH. If the pH effect predominated, that would explain the relatively high corrosion rates observed in solutions with pH 6.5. But this rationale

Table 21. Effect of Buffer Capacity at Different pH on the Corrosion of Mild Steel

	Alk	Cond. ($\mu\text{mho cm}^{-1}$)	β^*	Corrosion Rate† (mpy)	Dissolved Iron (mg/l)
pH = 6.5	50	85	49	19.9	1.70
	100	170	97	20.0	1.32
	200	300	195	27.5	0.82
	400	565	389	26.6	0.80

pH = 7.5	50	80	8	16.5	0.80
	100	165	16	19.9	0.56
	200	295	31	20.2	0.42
	400	555	64	22.7	0.36

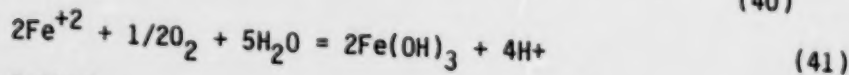
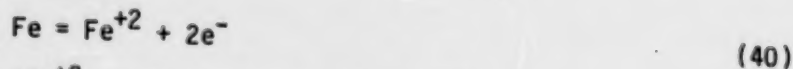
pH = 8.5	50	80	3	17.2	0.94
	100	160	5	20.9	0.71
	200	290	10	21.3	0.43
	400	550	20	24.8	0.37

*Buffer capacity in mg/l (as CaCO_3)/pH.

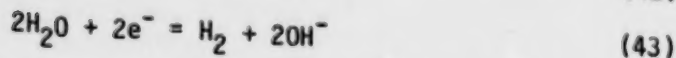
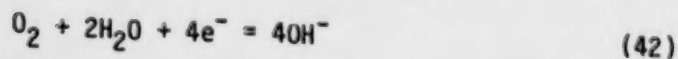
†Average of three corrosion rate measurements after 72-hour immersion time in an aerated system.

could not account for the increasing rates with increasing buffer capacities at pH 7.5 and 8.5. Other factors must be involved in the unexpectedly rapid corrosion in waters with relatively high buffer capacities. When the conductivity of the solution was considered, a positive relationship existed between corrosion rate and conductivity, that is, as more ions (Na^+ and HCO_3^-) were introduced into the aqueous system to raise the alkalinity to a desired value, the ionic conductivity increased which promoted faster corrosion rates. Therefore, the corrosion of mild steel at each pH value was related not only to buffer capacity, but also to conductivity or to a function involving both buffer capacity and conductivity. Figure 31 illustrates the variation of corrosion rate with the ratio $\beta/(\text{Cond})^{3/2}$. As the value of the ratio increased, the corrosion rate decreased. In other words, at constant conductivity, the corrosion rate would decrease with an increase in buffer capacity. When the buffer capacity is held constant and the conductivity is increased, the ratio is decreased corresponding to higher corrosion rates. Relating corrosion rate with $\beta/(\text{Cond})^{3/2}$ appears, therefore, consistent with the previous experimental result that increase in buffer capacity and alkalinity would contribute to lower corrosion rates. The inhibitive effect of buffer capacity can be understood better by recognizing the difference in the chemical mechanism of corrosion reactions of iron in water in the presence and absence of a buffer. According to Larson (90), the reactions taking place at the anode and cathode of the iron surface in the absence of a buffer are

Anode:



Cathode:



In the absence of bicarbonate, the usual half-cell oxidative and half-cell reductive processes occur respectively in the anode and cathode. Iron in the anodic region is oxidized to ferrous iron, which in turn is further oxidized by dissolved oxygen to form ferric hydroxide accompanied by release of hydrogen ions. In the cathodic area of the metal, either water

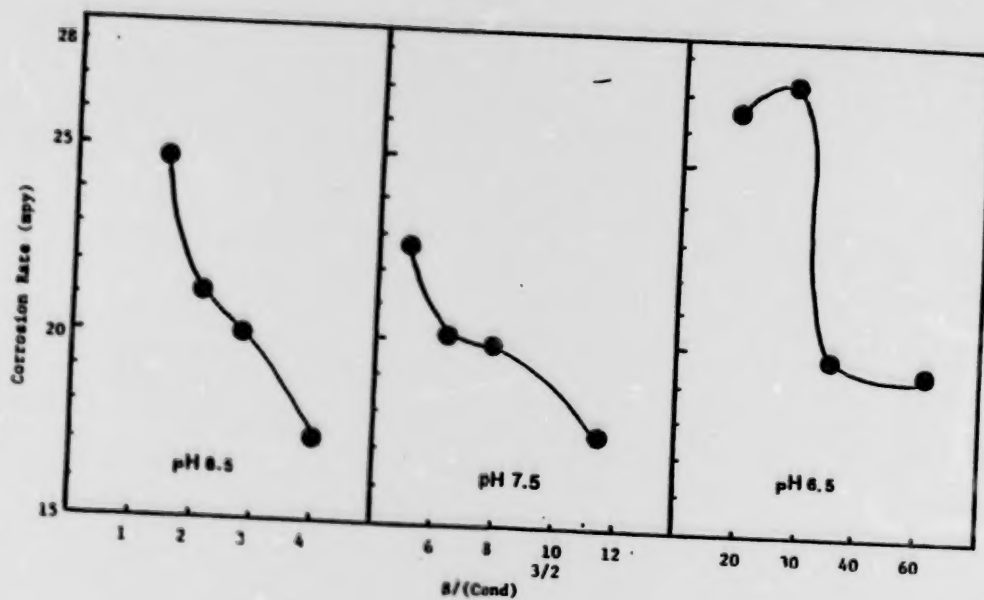
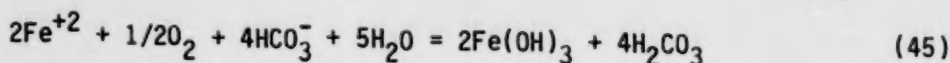
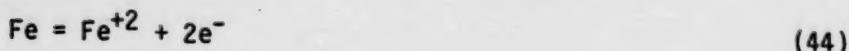


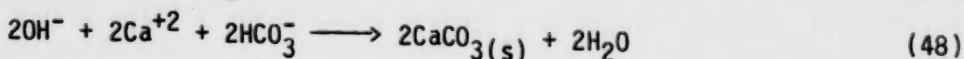
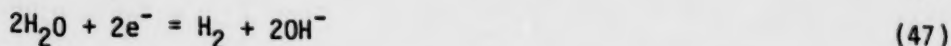
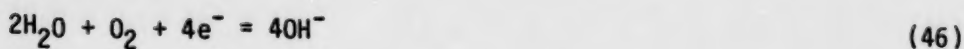
Figure 31. Relationship of Corrosion Rate of Mild Steel with the Ratio of Buffer Capacity (β) to Conductivity $3/2$.

is reduced to hydroxyl ions and hydrogen or oxygen is reduced to hydroxyl ions. When a buffer is present in the system, the following reactions occur.

Anode:



Cathode:



The oxidation of ferrous ion at the anode in the presence of HCO_3^- yields H_2CO_3 , a weak acid. At the cathode, an additional reaction consumes the hydroxyl ions by a neutralization process which leads to the deposition of CaCO_3 . Because of the additional calcite precipitation, the catholyte would not remain basic while the anolyte would not become as acidic as when Fe^{+2} is oxidized in the absence of HCO_3^- . This would prevent a significant pH differential, thus reducing the additional strong driving force of a concentration cell. With a bicarbonate-carbonate buffer system present and with sufficient amounts of calcium present, CaCO_3 deposition could produce a protective coating against further corrosive attacks.

Acceleration of Corrosion of Mild Steel Due to Dissolved Oxygen

One very important factor that was observed to affect corrosion was the presence of dissolved oxygen. As portrayed in the bar chart in Figure 32, the average corrosion rate of mild steel after 10 days in contact with five waters with different saturation indices all increased as the dissolved oxygen (DO) was raised from 1.5 to 5.0, then to 9.0 mg/l. For water "e" with SI = -2.12, the corrosion rate increased almost 200% when the DO increased from 1.5 to 5.0 mg/l. At DO = 9.0 mg/l, the overall increase was 328%. Comparable accelerating effect on corrosion was

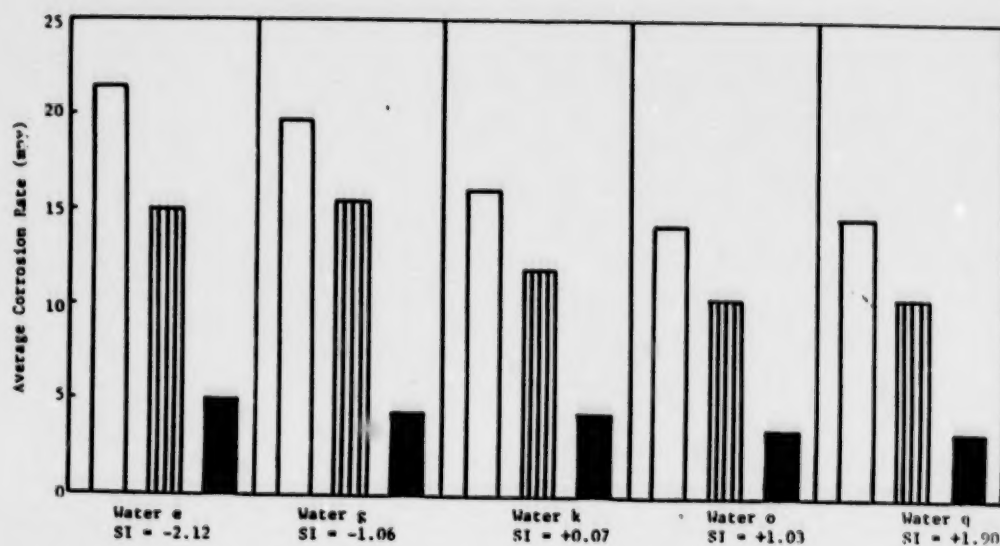


Figure 32. Bar Diagram Showing the Influence of Dissolved Oxygen on the Average Corrosion Rate of Mild Steel. The Concentration of Oxygen in mg/l are 9.0 ± 0.2 (), 5.0 ± 0.2 (), and 1.5 ± 0.02 ().

observed for water "q" with SI = +1.90. There was a two-fold increase in corrosion upon raising the DO to 9.0 mg/l. The acceleration of corrosion rate with increase in DO was due to the enhanced reaction rate occurring at both the anode and cathode sites on the metal. Irrespective of the presence or absence of a buffer system, increasing the amount of oxygen will increase the rate of the anodic oxidation of Fe²⁺ and cathodic reduction of H₂O as represented in equations 41, 42, 45 and 46. Thus, it is not surprising to learn that other workers have considered dissolved oxygen the controlling factor in the corrosion of iron and steel (91). The short-term studies of corrosion of steel by Cox and Roetheli (92) in waters with varying amounts of oxygen and the rate of corrosion curves for steel obtained by Lee (93) for waters with increasing oxygen pressure support the major role that oxygen plays in increasing the corrosivity of waters. Dissolved oxygen promotes oxygenation of ferrous ion which puts a stress on the Fe-Fe²⁺ equilibrium in favor of the Fe²⁺ release from the corroding metal. Stumm and Lee (94) investigated the oxygenation of ferrous ion and described the Fe(II) consumption in terms of a kinetic model where the rate was first order with respect to the concentration of both Fe(II) and O₂, and was second order with respect to hydroxide ion.

$$\frac{-d[\text{Fe(II)}]}{dt} = k [\text{Fe(II)}] [P_{\text{O}_2}] [\text{OH}^-]^2 \quad (49)$$

The research conducted by Jobin and Ghosh (95) has shown that the buffer capacity of a water has a definite influence on the oxygenation of Fe(II) when the buffer capacity is greater than 4 meq/L-pH. They proposed that for highly buffered bicarbonate solutions the rate law could be expressed as

$$\frac{-d[\text{Fe(II)}]}{dt} = k [\text{Fe(II)}] [P_{\text{O}_2}] [\text{OH}^-]^2 [\text{ }]^{1/2} \quad (50)$$

In both equations, (49) and (50), however, it is clear that an increase in oxygen concentration will enhance the oxygenation rate. On the other hand, if excessive amounts of dissolved oxygen are present protective oxide films could be more easily formed (96,97). These could saturate the metal surface and thus retard corrosion.

Effects of Water Quality on Corrosion of Mild Steel

The effects of the chemical composition of water on the rate of corrosion of mild steel in aerated systems is presented in Figure 33. The

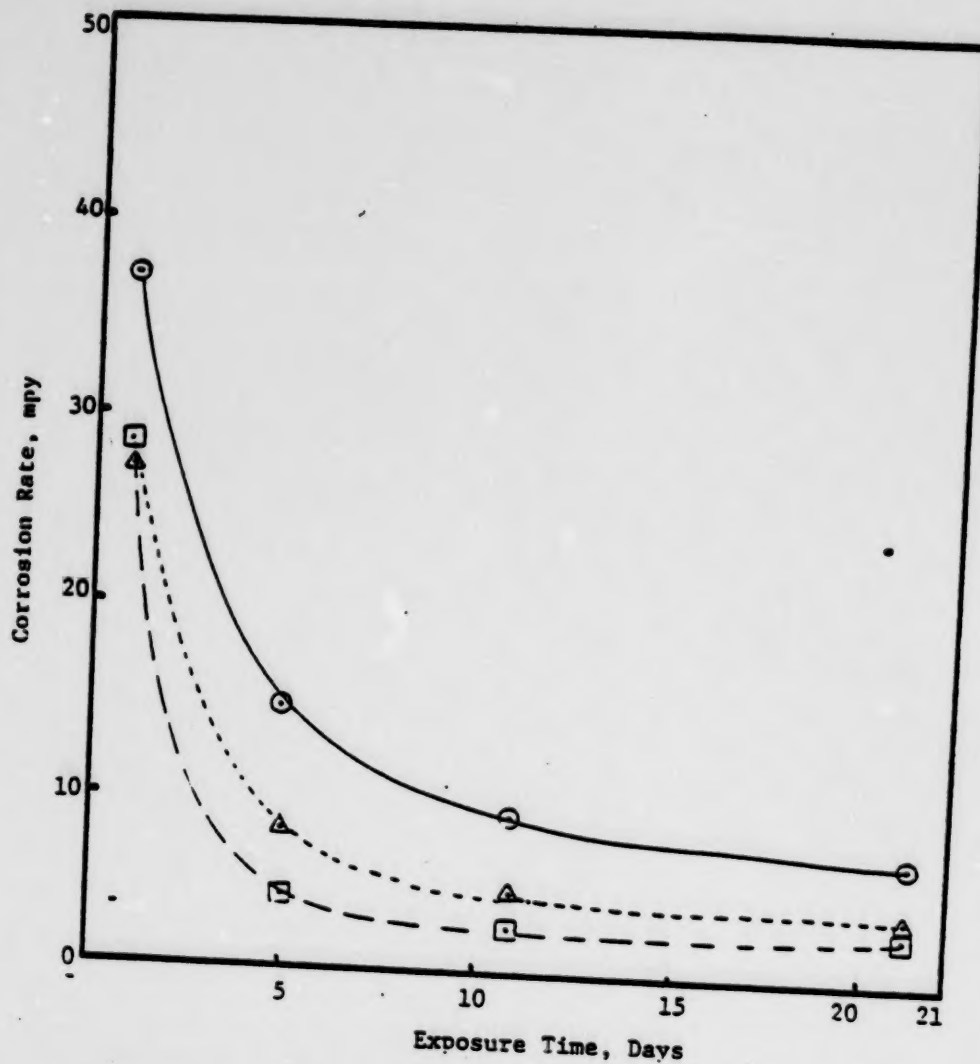


Figure 33. Effect of Chemical Composition of Aerated Water on the Rate of Corrosion of Mild Steel. pH 8.00, Chlorine Residual 1.5 mg/l, color 20 units.

- Water G
- △---△ Water H
- Water I

rate of corrosion of steel was found to be higher in Water G, than in either water H or I. Table 22 shows the composition of waters G, H, and I.

Table 22. Chemical Composition of Synthetic Waters

Parameter*	G	H	I
Ca ⁺⁺	20	40	60
Mg ⁺⁺	6	12	18
Na ⁺	23	46	69
Cl ⁻	36	71	107
SO ₄ ⁼	24	48	72
Alkalinity	50	100	150
Total Hardness	75	150	225

*All values are expressed in mg/L except alkalinity and total hardness which are expressed in mg/L as CaCO₃.

Figure 33 indicates that the chemical quality of water plays a major role in its corrosiveness towards a given metal. The differences in the rates of corrosion of a metal in waters of different chemical qualities can be explained in a number of ways. The difference in the mineral content of the waters, the concentration and type of ions, the buffering capacity of the water, dissolved oxygen, redox potential and pH all affect both the initiation and continuation of corrosion.

It should be pointed out that in most of the tests conducted, the initial rates of corrosion were often higher in hard waters than in soft waters. This may have been due to higher electrical conductivity of the hard water which would facilitate the initial corrosive attack. As the corrosion continued, the hard waters exhibited a lower corrosion rate due to precipitation of both calcium carbonate and other corrosion products. It was also observed that the corrosion product was more firmly attached to the corroding metal in hard waters than in soft waters.

Another factor of significance is the solubility of chemical species in solution. A water of higher mineral content tends to precipitate some chemical constituents more readily than waters that are low in such minerals. The inhibitory action of the precipitation of calcium carbonate,

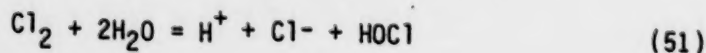
for example, has been well documented as detailed by Merrill and Sanks (53) and other (90,98). Chloride and sulfate ions have been shown to accelerate the rate of corrosion, while carbonate, hydroxyl, phosphate and silicate tend to form insoluble compounds that are adsorbed or deposited on the metal surface and thus impede the rate of attack.

Chlorine Residual:

The effect of chlorine residual on the rate of corrosion of mild steel is presented in Figure 34. It shows that the presence of a 1.5 mg/L free chlorine residual had a positive effect on the rate of corrosion of mild steel in both aerated and deaerated solutions.

Difficulties were encountered in maintaining a constant chlorine residual throughout the test period. Chlorine had to be added to the test solutions periodically. The instability of chlorine in water for prolonged times is indicative of its tendency to take part in corrosion reactions. Chlorine as a strong oxidizing agent is reduced to chloride ion. Its reduction promotes the oxidation of the metal.

Chlorine can accelerate the rate of attack of iron either by direct increase of the redox potential of the electrolyte that favors the dissolution of iron to ferrous and ferric ions, or through a sequence of chemical reactions that produce hydrogen ions, hypochlorous acid, hypochlorite ions and chloride as shown below:



Volkering (99) showed that chlorine dosage in the range of 0-4 mg/l increased the rate of corrosion of mild steel in seawater. Similar effects of chlorine were reported by Larson (100) for potable waters. Larson noted that the rate of corrosion of steel increased when free chlorine concentration was 0.4 mg/l or greater. Combined chlorine in the form of NH_2Cl was shown to exert an inhibiting effect on the rate of corrosion of steel when present at concentrations of 0.4-3.6 ppm as Cl (101).

The effect of chlorine, like that of oxygen, diminishes after the corroding surface is passivated with corrosion by-products.

Natural Color:

The presence of natural color at levels of 15 and 20 platinum-cobalt units (PCU) on the corrosion of mild steel was evaluated in a series of experiments. It was found that increasing color had a negative effect on

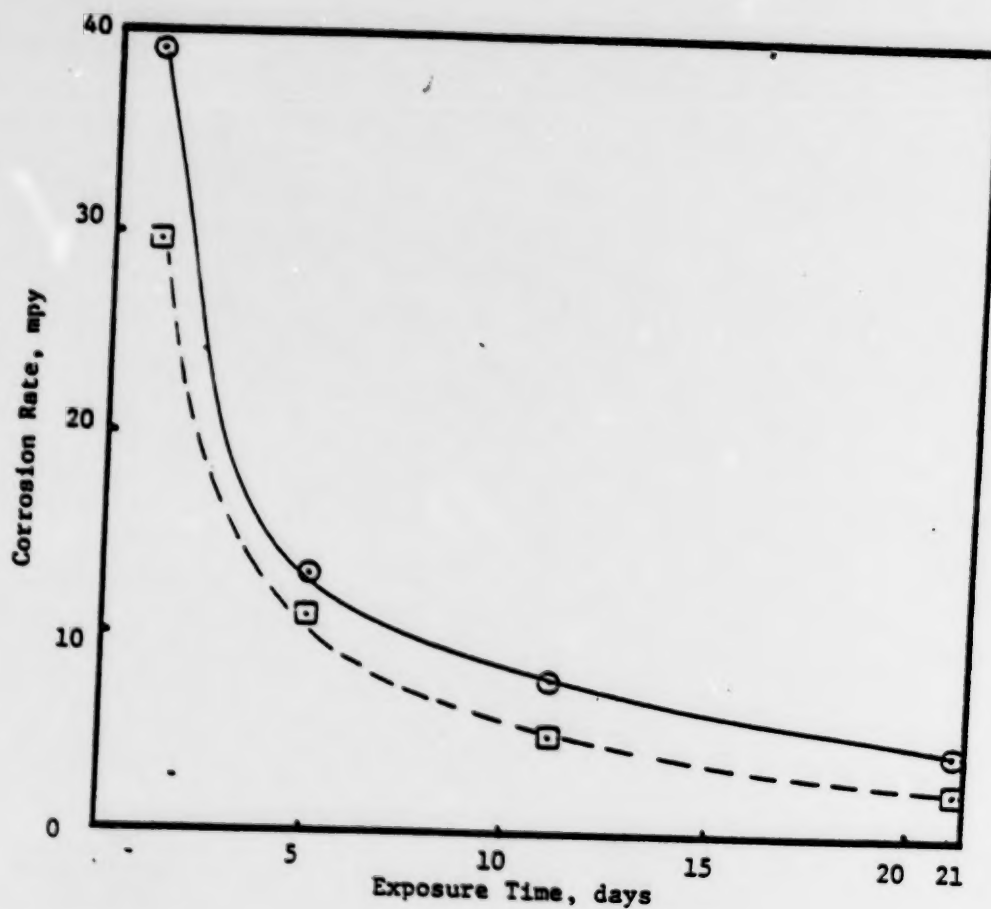


Figure 34. Effect of Chlorine Residual on the Rate of Corrosion of Mild Steel in Hard Water. pH 8.00; No Color Added

○ — ○ Chlorine = 1.50 mg/l
□ - - - □ Chlorine = 0.00 mg/l

the rate of corrosion of steel (Figure 35). Furthermore, it was observed that most of the color was coagulated and was removed from solution by corrosion products.

Larson (90) reported a significant decrease in the rate of corrosion of cast iron specimens in the presence of 2 PCU of extracted color in a limited number of tests. The difference in the color tests in various studies may be due to the type and the nature of the color. According to Christman and Ghassemi (102), organic color in natural waters is comprised of complex polynuclear molecules derived from decayed natural plants, and has acidic properties.

Effect of Specific Ions

Although most drinking waters contain the major cations and anions, their concentrations vary greatly from one supply to another. Several experiments were conducted to evaluate the effect of specific ions such as chloride and sulfate, and their associated cations on the corrosion of mild steel. The findings of these tests are summarized below.

Chloride ions

A number of short-term experiments were conducted on the corrosion of mild steel. Three chemical compounds containing chloride (NaCl , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) were tested at four different concentrations, ranging from 10 mg/l to 160 mg/l of chloride ion. Both weight loss and Corrator probes were used to measure the rates of corrosion. The pH in some of the tests was adjusted to 8.40 using a sodium borate buffer, while no attempt was made to adjust the pH in others. All tests were aerated. The results of the chloride tests are shown in Figures 36 and 37.

The rates of corrosion of mild steel increased with increasing concentrations of chloride ion, and were generally not affected by the type of cation. The rates, however, were somewhat higher in unbuffered solutions compared to those to which sodium borate was added as a buffer.

The corrosion rates as determined by the two methods were generally in good agreement. The mechanism of corrosion by chloride ion has been well documented elsewhere (90,103). The point to be made here is that in the presence of oxygen, the ferrous ion is oxidized to ferric hydroxide. This results in the formation of hydrochloric acid in accordance with the following chemical reactions:

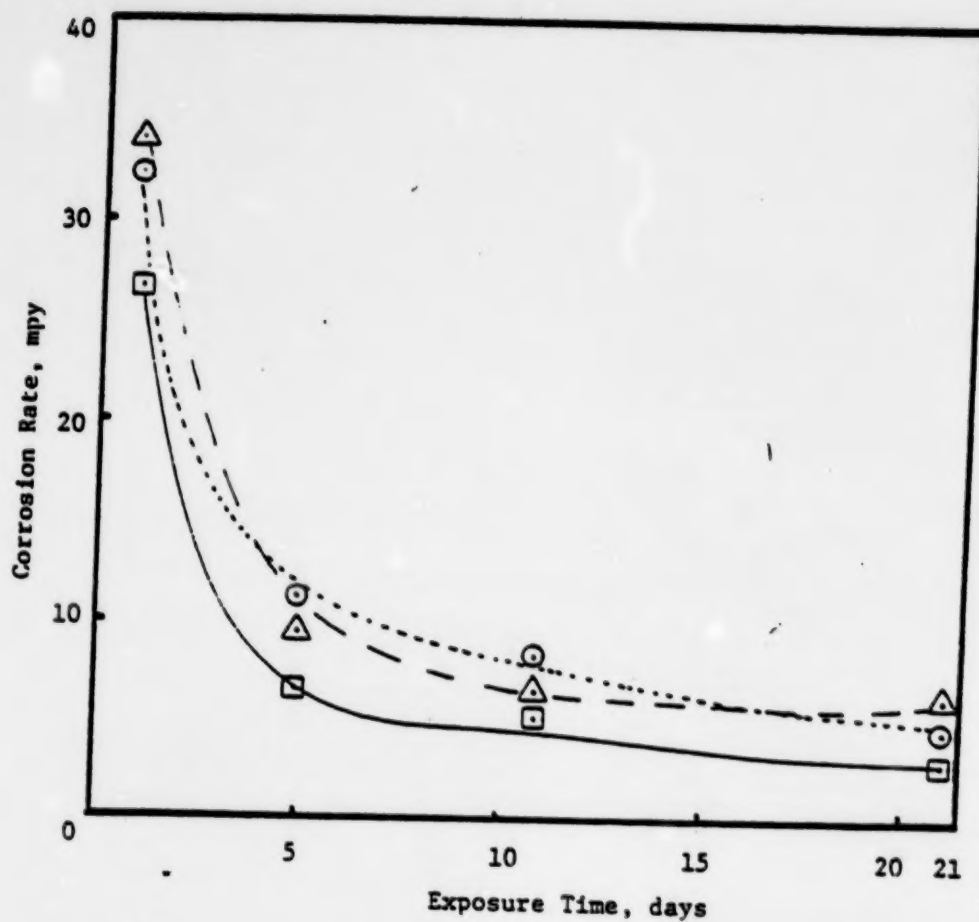


Figure 35. Effect of Color on the Corrosion of Mild Steel in Hard Water, pH 8.00. Chlorine Residual 1.00 mg/l

- No Color
- △ 15 Color Units
- 20 Color Units

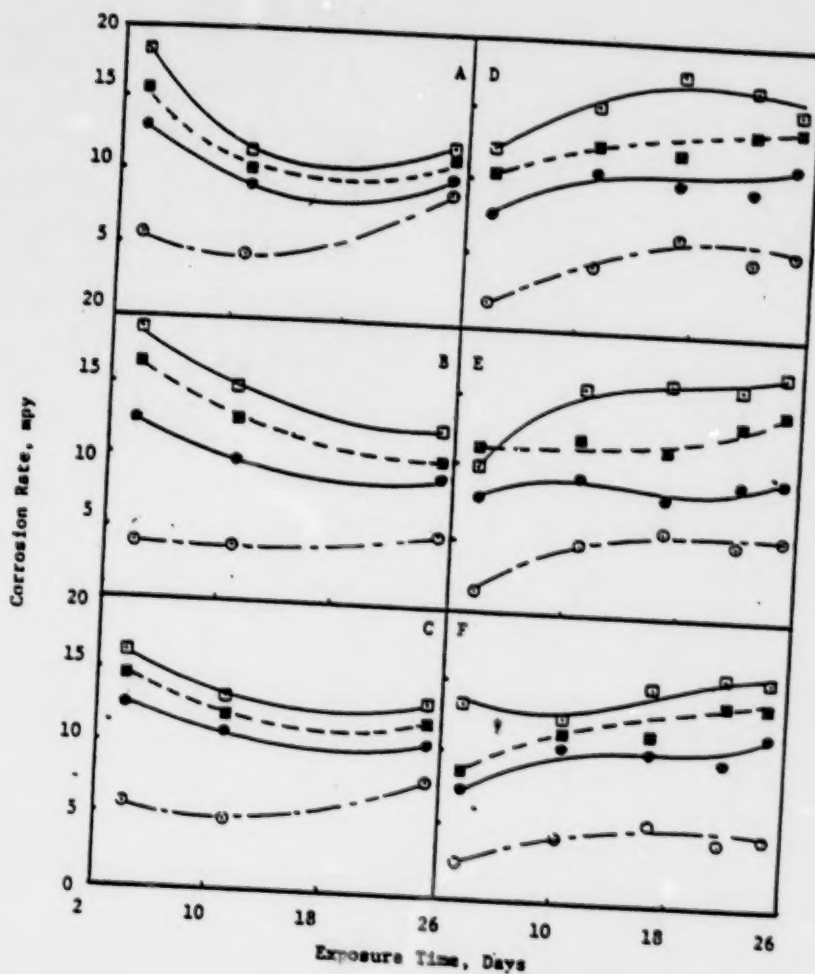
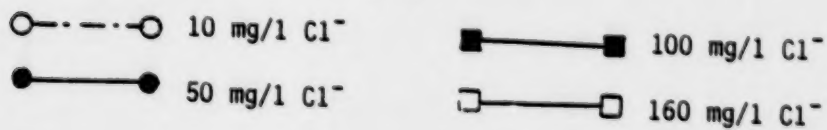


Figure 36. Effect of Chloride on the Rate of Corrosion of Mild Steel at pH 8.40. A, B, C Weight Loss. D, E, F Corrator. A, D NaCl; B, E CaCl₂; C, F MgCl₂.



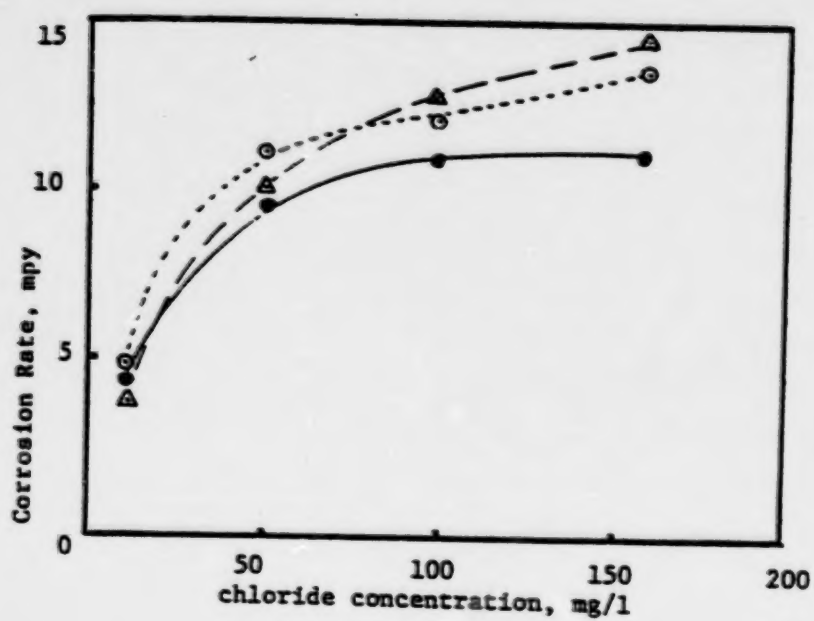
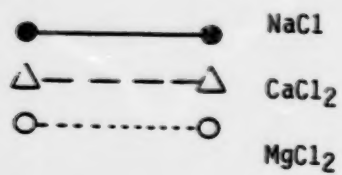
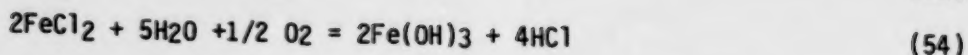
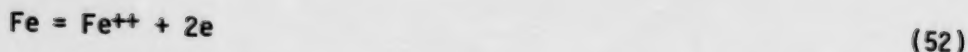


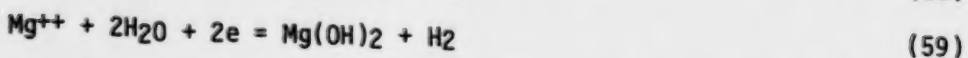
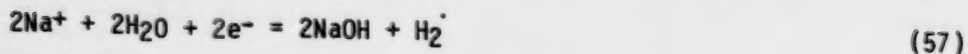
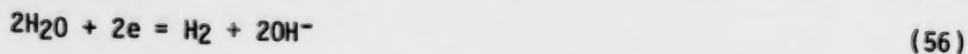
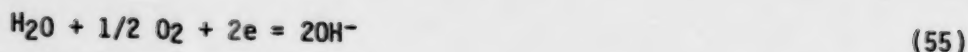
Figure 37. Effect of Chloride ion on the Rate of Corrosion of Mild Steel in Aerated Solutions. pH 7.18, Exposure Time 11 Days



Anode:



Cathode:



The aggressivity of chloride ion is largely due to its ability to form soluble ferrous compounds and thus generate hydrogen ions by reaction with water. This lowers the pH at the anode. This differential in pH between the anode and the cathode promotes the rate of corrosion by causing a potential gradient between the anodic and cathodic sites.

Equations 57-58 present the reactions at the cathode caused by the salts of NaCl, CaCl₂ and MgCl₂ respectively. The right side of these equations indicates OH⁻ formation which would raise the pH at the cathode, thus causing a further increase in the rate of corrosion.

Chloride ion has been particularly noted for the breakdown of passivity in many ferrous alloys and it is considered as one of the main causes of pitting in stainless steels (104). Similar results were reported by Hatch and Rice (105), that is, increasing chloride concentrations had a positive effect on the rate of corrosion of steel.

Sulfate Ions

The effect of sulfate ion on the rate of corrosion of mild steel was investigated using three different sulfate salts (Na₂SO₄, CaSO₄, and MgSO₄·7H₂O). The pH of the sulfate solutions and the concentration of sulfate ions were similar to those of the chloride tests. The rates of corrosion of steel, as affected by sulfate ion, are presented in Figures 38

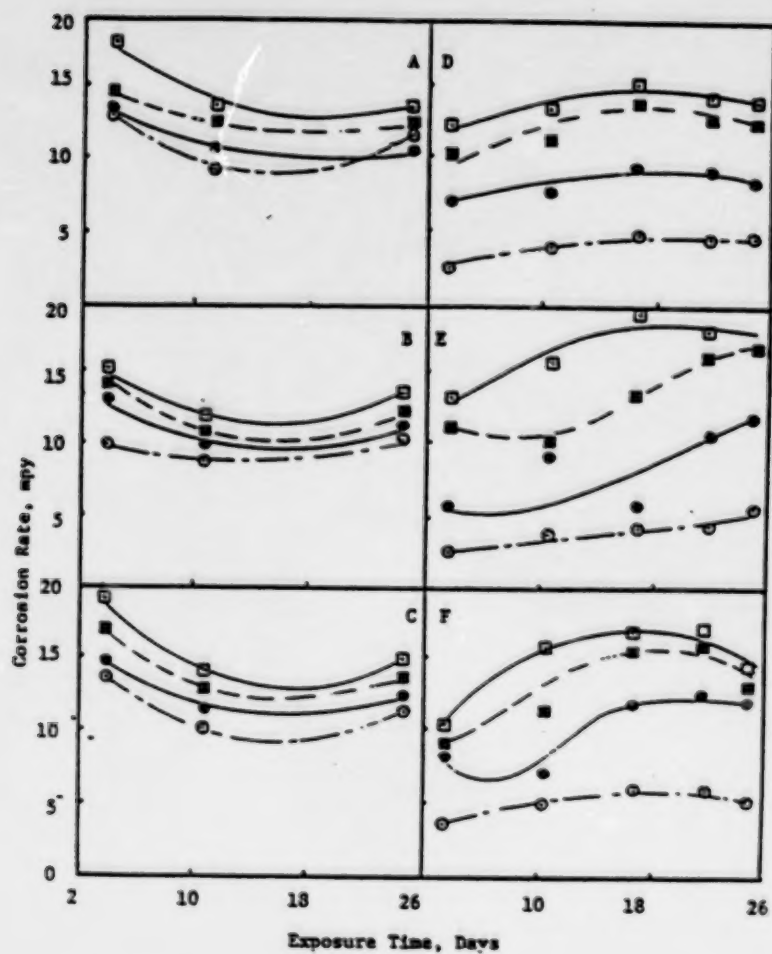
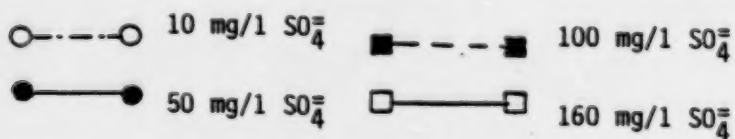
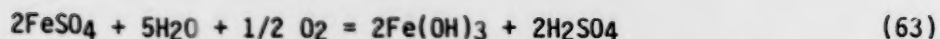
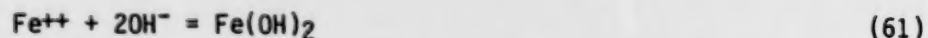
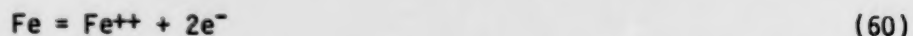


Figure 38. Effect of Sulfate on the Rate of Corrosion of Mild Steel at pH 8.40. A, B, C Weight Loss. D, E, F Corrotor. A, D Na_2SO_4 ; C, F MgSO_4 .



and 39. The average rates of corrosion of steel in both chloride and sulfate solutions are included in Table 23.

In a separate series of tests, the concentrations of chloride, or sulfate ions were added at 10, 50, 100 and 160 mg/l as in previous tests, but the solution contained all three cations Na^+ , Ca^{++} , and Mg^{++} . The resulting rates of corrosion are summarized in Figure 40 and Table 24. The rates of corrosion of steel were not affected by any of the cations studied. The corrosion rates as determined by the weight loss and Corrotrator methods were found to be generally in good agreement. As can be seen, the rates of corrosion increased with increasing concentrations of both chloride and sulfate ions. The mechanism of the increased rate of corrosion of iron by sulfate ions is similar to that of chloride ions. In the absence of dissolved oxygen, the anode will contain ferrous sulfate and ferrous hydroxide. When dissolved oxygen is present, the ferrous ion is oxidized to ferric hydroxide and sulfuric acid is formed (90). The production of H_2SO_4 (Eqs. 60-63) will lower the pH at the anode, while the pH at the cathode would be increased by the cathodic reactions (Eq. 56-59). This difference in pH would increase the redox potential which would result in the accelerated rate of attack of steel specimens.



In a 5-day test, Hatch and Rice (105) showed that the rate of corrosion of steel in sulfate solutions was substantially higher than in chloride solutions of same anion concentrations.

Redox Potential:

Redox potential is an important parameter in electrochemical corrosion. The response of a platinum electrode for measuring the redox potential, E_H , in a corroding system is presented in Figure 41. This

Table 23. Effect of Chloride and Sulfate on the Rate of Corrosion of Steel in mpy at pH 8.40. Weight Loss Method.

No.	Chemical Compound	Cl ⁻ or SO ₄ ⁼ mg/l	Corrosion Rate, mpy		
			4 days	11 days	25 days
1	NaCl	10	5.9	4.5	8.9
2		50	13.4	9.7	10.5
3		100	16.0	11.1	11.6
4		160	19.3	11.2	12.4
5	CaCl ₂ ·2H ₂ O	10	4.3	4.0	5.1
6		50	13.2	10.2	10.3
7		100	17.2	12.7	9.4
8		160	19.6	14.8	12.5
9	MgCl ₂ ·6H ₂ O	10	6.2	5.2	8.3
10		50	13.0	11.3	10.7
11		100	15.7	12.4	12.1
12		160	16.5	13.3	13.7
13	NaSO ₄	10	13.4	9.0	11.8
14		50	13.4	10.1	10.7
15		100	14.3	12.5	12.6
16		160	18.2	13.0	12.9
17	CaSO ₄	10	10.4	9.0	10.5
18		50	12.9	9.7	11.0
19		100	14.5	11.0	10.7
20		160	14.6	12.0	13.1
21	MgSO ₄ ·7H ₂ O	10	14.2	10.1	11.7
22		50	15.2	11.2	11.9
23		100	17.4	12.8	14.1
24		160	19.5	13.5	15.0

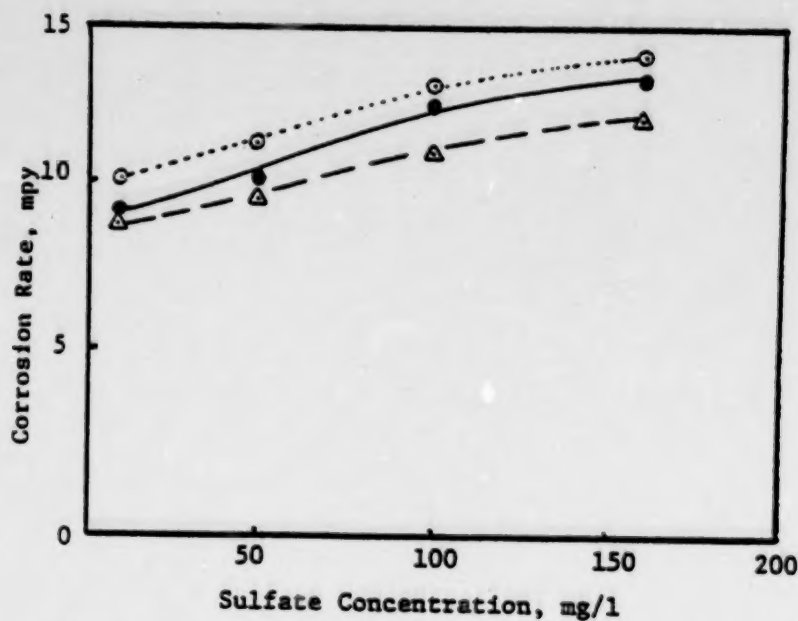


Figure 39. Effect of Sulfate Ion on the Rate of Corrosion of Mild Steel in Aerated Solutions. pH = 7.23, Exposure Time 11 Days

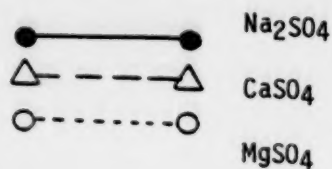


Table 24. Average Rate of Corrosion of Mild Steel in Chloride and Sulfate Solutions.

Chemical Compounds	Anion Concentration (mg/l)	Corrosion Rate, mpy		
		4 days	11 days	25 days
NaCl + CaCl ₂ · 2H ₂ O + MgCl ₂ · 6H ₂ O	10	6.6	9.0	10.4
	50	13.0	9.9	12.7
	100	15.3	11.8	13.0
	160	18.0	15.6	15.6
Na ₂ SO ₄ + CaSO ₄ + MgSO ₄ · 7H ₂ O	10	12.4	7.2	8.1
	50	13.3	9.4	10.1
	100	15.6	9.8	10.8
	160	19.8	15.4	11.9

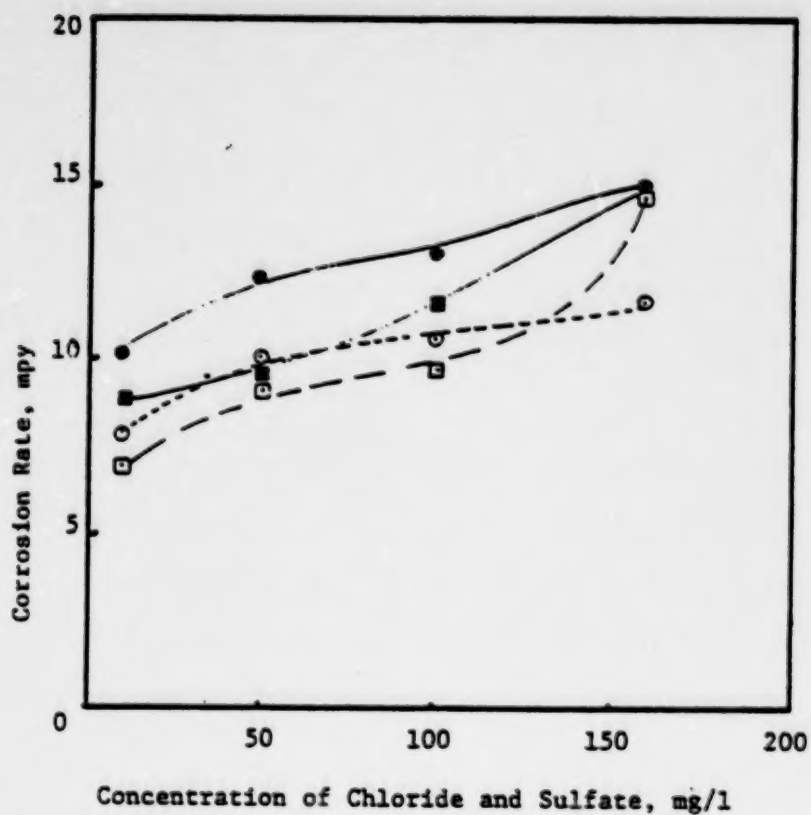


Figure 40. Effect of Chloride and Sulfate on the Rate of Corrosion of Steel in Aerated Solutions Containing Ca^{++} , Mg^{++} and Na^{+} ions. pH 7.28

- — ● Chloride, 25 days
- — ■ Chloride, 11 days
- - - - ○ Sulfate, 25 days
- - - - □ Sulfate, 11 days

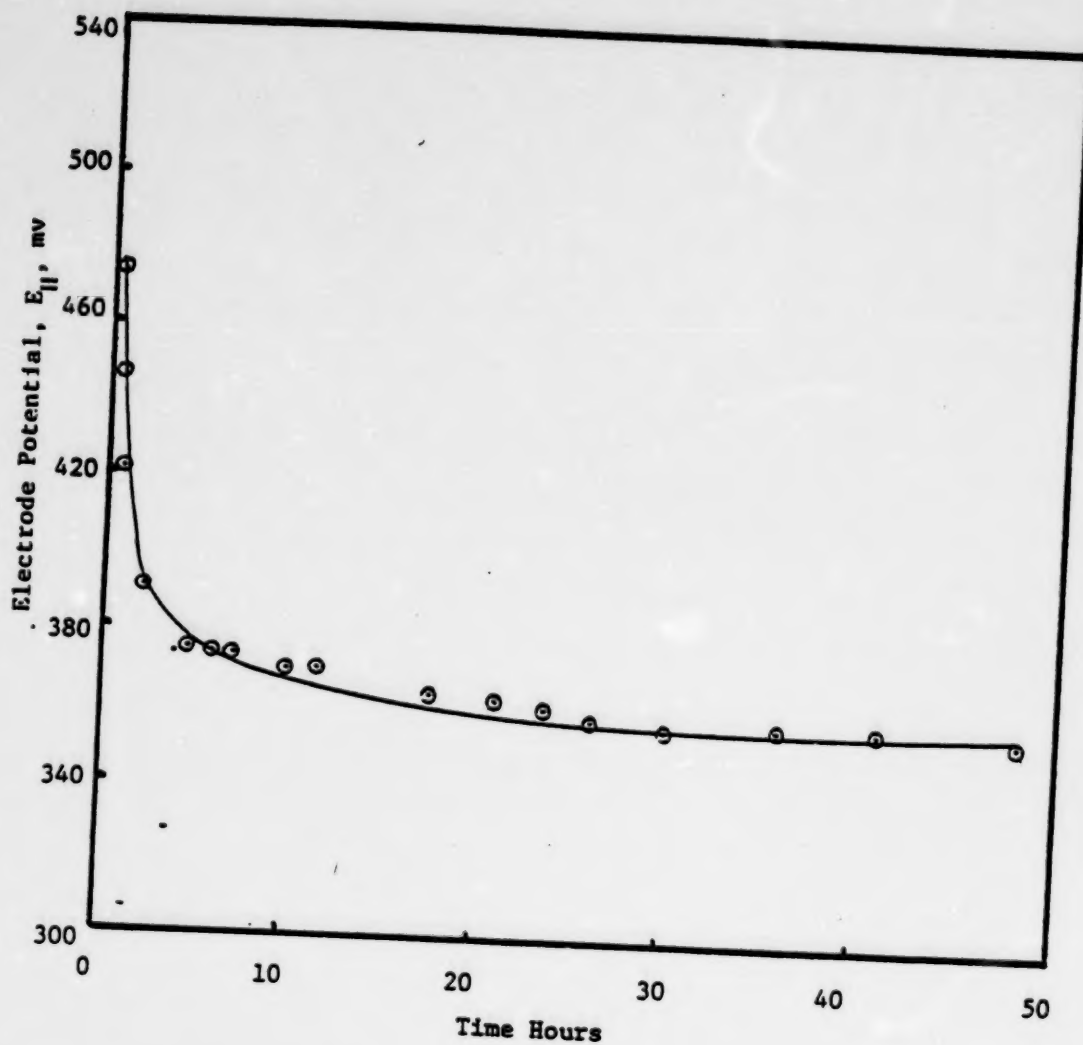


Figure 41. Electrode Response in a Typical Mild Steel Corrosion System. pH 8.10

indicates that several hours were required to establish a steady state condition before an E_H value could be measured accurately. The measured E_H values in water H were plotted on the E_H - pH diagram (Figure 42). All values coincided with a thermodynamically passive region. This indicates that if aggressive ions such as chloride and sulfate are excluded from the solution, the metal surface will form a passive film. As long as the film is maintained, corrosion will be drastically reduced.

Electrode potential measurements in drinking waters should be interpreted with care as pointed out by Morris and Stumm (106). Some of the reasons are: (1) Most redox reactions in drinking waters are slow and may not reach the state of a reversible equilibrium. (2) Several cations, anions, and gases which are usually present in any drinking water contribute to the measured E_H values. This causes the measured potentials to be mixed potentials which are difficult to quantify. (3) The measured E_H values in the bulk of the solution may be entirely different from the actual E_H at the surface of the corroding metal. (4) Corroding systems are dynamic systems where both dissolution and precipitation reactions are taking place simultaneously.

Despite these limitations, redox potential measurement and Pourbaix diagrams provide useful information for understanding the thermodynamic behavior of a given metal in an aqueous system (11). As Figure 41 indicates, the E_H values after immersion declined fairly rapidly during the first several hours which may suggest that, (a) redox measuring electrodes were in the process of establishing equilibrium with the species in solution, and (b) that the declining E_H values showed the onset of corrosion as opposed to passivation. As corrosion continued for a number of days, the E_H values tended to increase gradually, indicating that passivation of the iron was taking place. The degree of passivity largely depended on the presence of oxygen, the type of passivating ions and the quality of adsorbed or deposited film on the metal surface.

In addition to E_H , the conductivity of selected solutions was measured during the experiments. Since the conductivity of a given solution is a gross measure of the ability of that solution to conduct electrical current, it plays a major role in initiation of corrosion attacks by completing the electrical circuit in the corrosion cell. Once the metal surface is coated with impervious corrosion by-products, the role of conductivity, however, becomes minor.

The rates of corrosion increased with increasing Cl^- , SO_4^{2-} , Na^+ and Mg^{++} ions when the solution did not contain any carbonate alkalinity. The rates of corrosion were found to be substantially lower in the presence of

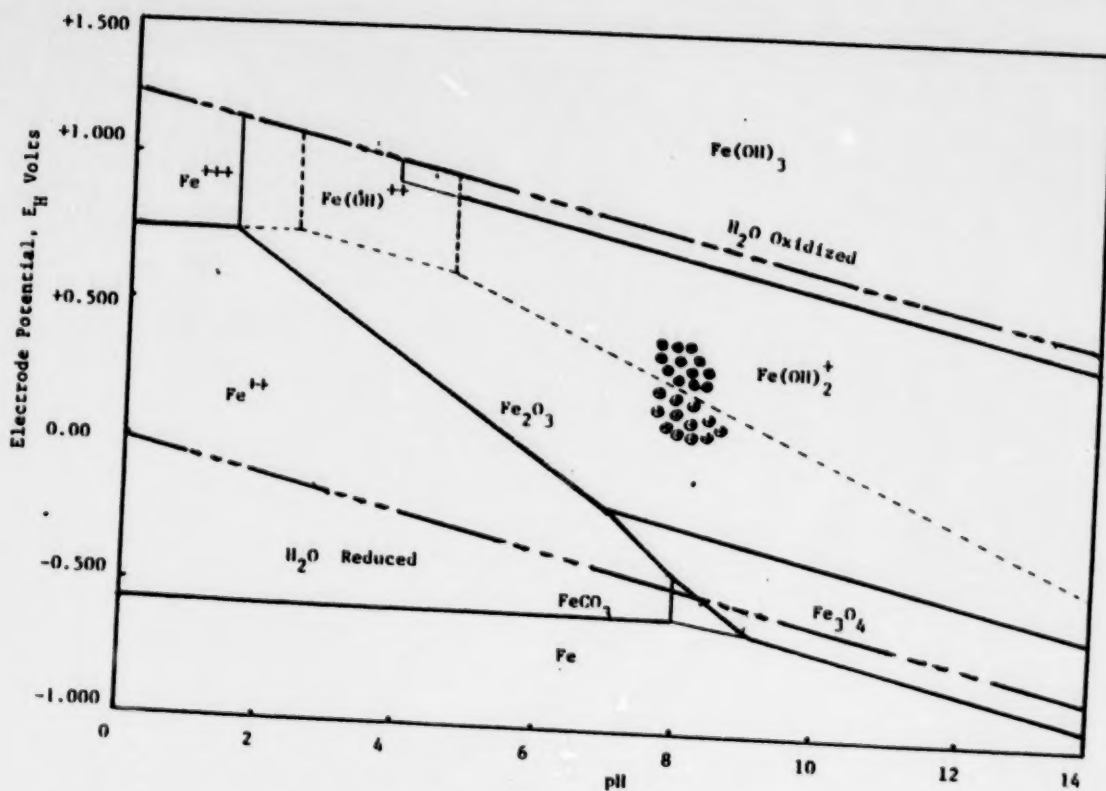


Figure 42. Pourbaix Diagram for 5×10^{-6} M Fe in the Presence of 100 mg/l Alkalinity as $CaCO_3$, with Measured E_H Values.

● Aerated

⊕ Deaerated

carbonate alkalinity, even when the solution conductivities were high.

It appears that the type of minerals present in solution are major factors in reducing or enhancing the rates of corrosion.

Variation in Water Quality

Two types of tests were performed. In one series of tests, the experimental water quality variables were frequently readjusted to their initial values, while in the other no such attempt was made. The water quality parameters were monitored in both cases.

Of all the parameters monitored, the concentrations of Na^+ , Mg^{++} , Cl^- , and SO_4^{--} remained relatively constant throughout the exposure period. The pH of the solutions changed rather quickly and required frequent adjustments. The greatest instability in pH values was observed in waters of low buffer capacity and low ionic composition.

The concentrations of alkalinity and calcium ion were both affected by the exposure time under both aerated and deaerated conditions. The change in alkalinity was very pronounced in hard waters compared to soft waters. This was consistent with the experimentally determined corrosion rate values where an appreciable amount of alkalinity precipitated with calcium in hard waters. This may have been in part responsible for the lower rates of corrosion experienced in hard waters compared to those in the soft waters.

The results of the iron pickup by the solutions are shown in Figure 43. The initial concentration of iron was 0.0 mg/L. The maximum concentrations of total soluble iron occurred after about 24 hours of exposure in all aerated waters, after which it decreased progressively as the experiments continued. This reduction in the concentration of iron could be explained in a number of ways: (1) decrease in the rate of corrosion with time, (2) precipitation of hydrated ferric oxide by reaction of dissolved iron with oxygen, and (3) lower solubility of ferric oxide.

On the other hand, the deaerated systems picked up only small quantities of iron as the result of lower rates of corrosion. The anodic reaction was stifled by the elimination of dissolved oxygen from the water.

For aerated systems at the initial stages of corrosion, waters H and I picked up more iron than water G, while this difference became minimal after two weeks of exposure. In the deaerated systems, water G picked up slightly more iron than the hard waters, possibly due to the effect of low buffer capacity.

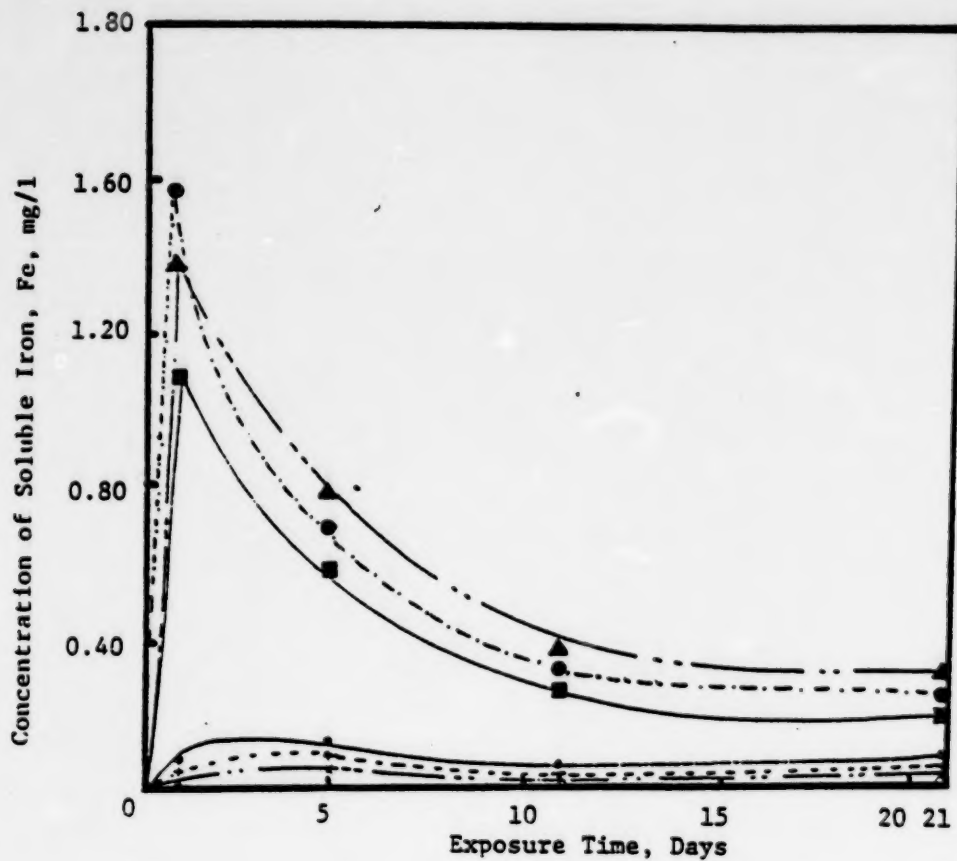


Figure 43. Changes in Concentration of Soluble Iron Due to the Action of Corrosion, pH 8.00.

- Water A, Aerated
- ▲ Water B, Aerated
- Water C, Aerated
- × Water A, Deaerated
- + Water B, Deaerated
- Water C, Deaerated

The Nature of Corrosion

From laboratory observations, it may be concluded that the corrosion of mild steel was usually of the "general type", covering the entire surface of the metal exposed to the solution. Occasionally, only a part of a coupon corroded preferentially, while the rest of the coupon did not show any signs of corrosion. Corrosion in such cases was also of the "general type".

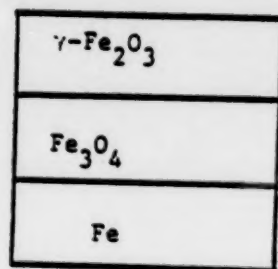
One reason for the absence of pitting corrosion in the tests was probably the duration of the tests. Pitting normally requires an induction period for nucleation and then a longer exposure time for propagation.

The corrosion of steel and cast iron in distribution systems is either "general" or "localized". One type of localized corrosion, referred to as tuberculation when oxygen is present, is a type of pitting in which an active pit is covered by growing mounds of corrosion products. This reduces the pipe size and increases the roughness of the inside surface of the pipe, thereby restricting the flow of water significantly. In extreme cases of tuberculation, there is total blockage of the pipe.

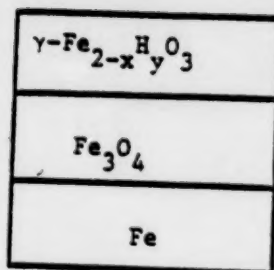
The occurrence of pits is common in those metals that display active-passive transition. To understand how and why pitting takes place, a brief review of passivity is in order.

Passivity is a condition that is due to the formation of a protective film of oxide or other chemical species on the metal surface, which renders the metal more noble and therefore results in reduced corrosion. The nature and type of such films depend on the type of metal and the type of dissolved ions and gases in solutions. There is still a great deal of controversy concerning the mechanism of formation of such films and their morphology.

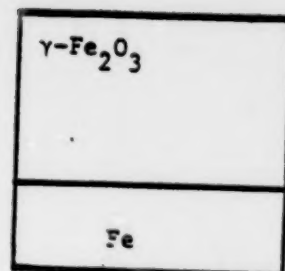
According to Cohen (107), there has been little change in the basic theories of passivity since they were proposed almost 150 years ago. The two basic theories of passivity are: (1) the oxide film theory, and (2) the electronic change in the metal (107). A modification of the latter theory is the adsorption theory (7), in which passivity is explained as being induced by chemisorption of oxygen on the metal surface. The formation of passive films has been suggested (107) to result from heterogeneous reactions between the metal and solution including adsorption, anodic dissolution and precipitation. Several models have been proposed (107) for the structure of these passive films on iron surfaces as indicated in Figure 44. The main difference among these models is attributed to the presence or absence of water or hydrogen in the films.



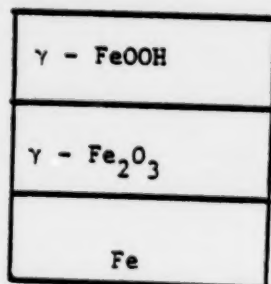
(A)



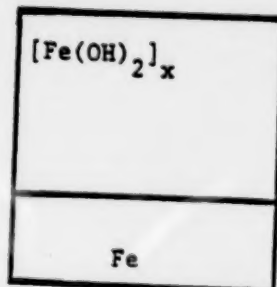
(B)



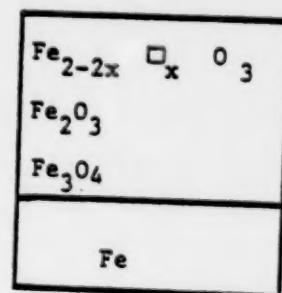
(C)



(D)



(E)



(F)

Figure 44. Proposed Models of Passive Films on Steel (261)

(A) Cubic Oxide Film

(B) Inclusion of Water or Hydrogen in Model A.

(C) Passive Film in Acid Solutions

(D) Passive Film in Neutral Solutions

(E) Hydrated Polymeric Oxide Film

(F) Cation Deficient Film

Figure 44B, for example, is a modification of the cubic oxide film by including hydrogen or water in the film. Model C (Figure 44) has been proposed in acid solutions, while Model D has been suggested in neutral solutions (107). The difference between Models C and D is the presence of δ -FeOOH, the solubility of which is affected by the pH of solution. Form E is a hydrated polymeric oxide film and model F is a cation-deficient oxide film observed in borate solutions (106).

It is believed that oxide films are semiconductors and that vacancies, hydrogen, water and the type of metal and solution play important roles in the morphology and modification of such films (106).

Pitting is caused by the local breakdown of passive films. Greene and Fontana (6), in a critical review of pitting concluded that Cl^- , Br^- and ClO_4^- are the most important anions that cause pitting. They further noted that oxidized metal halides, such as ferric, cupric and mercuric halides caused more pitting than non-oxidized metal halides, such as calcium, aluminum, and sodium halides. Kolotyrkin (108), listed several other factors that cause pitting, in addition to the ones described by Greene and Fontana (6). Bromide ion and dissolved oxygen in the presence of halide ions were mentioned. Other factors included the structure and physical state of the metal surface, the rate of diffusion of aggressive anions, the extent and conditions of cathodic reactions, and the anode-cathode area ratio (108). With regard to the theories of pitting, Kolotyrkin (108) concluded that: (1) pits are formed at the anodic sites, primarily due to increased acidity at the anode, and (2) that pits are caused by the displacement of passivating dissolved oxygen by aggressive anions.

Galvele (109) on the other hand presented several theories of pitting, namely: (1) oxide film defects of the metal surface, (2) ion migration and contamination of the oxide film, (3) competitive adsorption between passivating and non-passivating species, (4) critical concentration of aggressive anions, (5) salt film formation on the metal surface, and (6) localized acidification of the metal that interferes with the repair of the passive films. Galvele (109) further emphasized the significance of pitting potential¹, the role of nucleation sites such as sulfide and other non-metallic inclusions, and the effect of alloying elements. The effect of aggressive ion concentration on the lowering of pitting potential, E_p , was reported further to have the following relation

¹ The potential above which pitting initiates on the metal surface and below which the metal remains passive.

$$E_p = A - B \log C$$

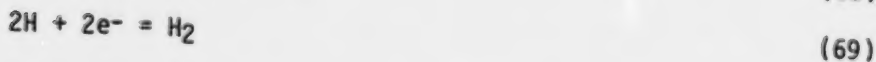
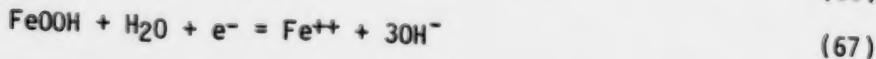
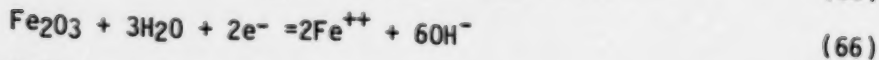
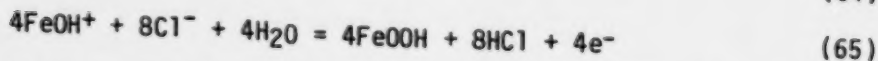
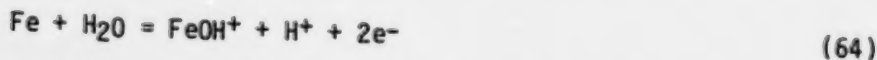
where A and B are constants, and C is the concentration of the aggressive anion. He noted that pH did not affect the pitting potential of the metal. It may be concluded that pitting occurs in two stages. Nucleation of pits on a passive surface, followed by propagation into an active pit (110,111). Wranglen (110) noted that in carbon steels, pits initiate at the sulfide inclusions. The nucleation of pits whether due to flaws in the oxide films (109) or by competitive adsorption and displacement of passivating species (108,109,111) by aggressive anions, leads to the rupture of the passive films and ultimately the development of deeper pits.

The effect of chloride on the breakdown of passive films, and some of the reactions that make pitting possible are illustrated in Figures 45 and 46 respectively (107,112).

Figure 45 shows the dual role of water in either film formation or its displacement by chloride ion. Figure 45 A shows the metal ion that is produced anodically at a site of an oxide defect is contained in the gel-like hydrated passive film. In the absence of chloride ion (Figure 45 B), the dissolved metal ions form a film through bridging of OH bonds (112). When chloride is present in solution, it interferes with the bridging action by replacing water molecules (Figure 45 C).

The film is finally ruptured by the penetration of chloride ion resulting in release of dissolved metal ions (Figure 45 D).

The general reactions (Eqs. 64-69) involved in the breakdown of passive films as described by Cohen (107) are summarized as



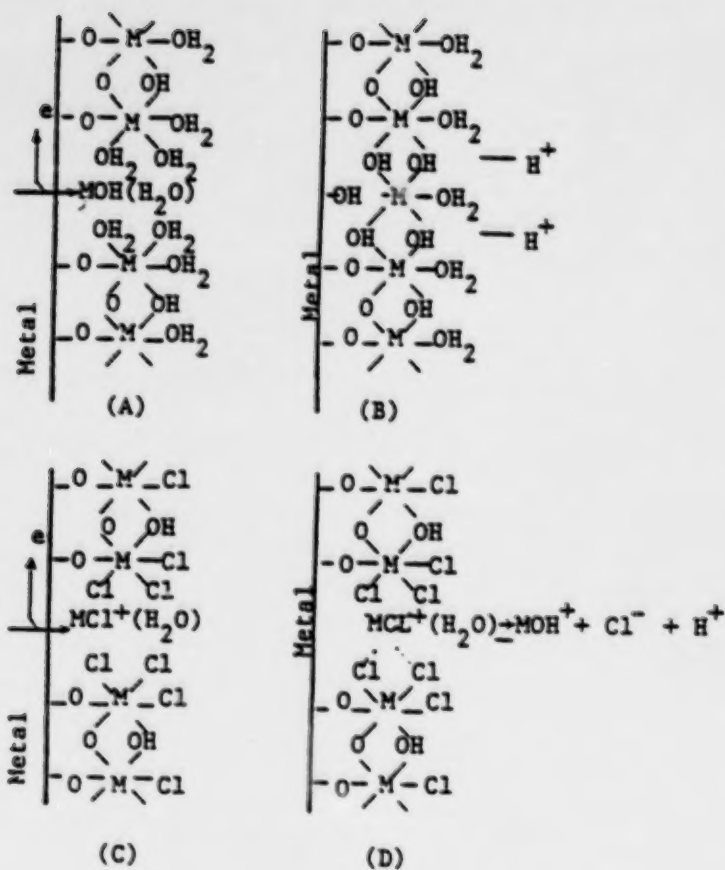


Figure 45. Schematic Diagrams of the Breakdown of a Passive Film by Chloride Ions. (A) Dissolution of Metal (B) Film Formation Due to Hydrogen Bonding (C) Replacement of Water by Chloride Ions (D) Film Breakdown (112)

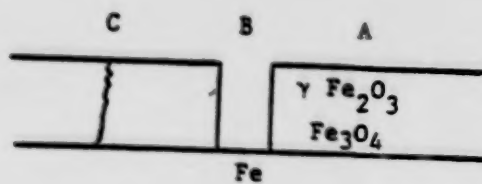
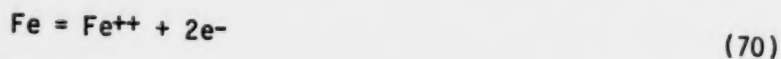


Figure 46. Breakdown of Iron Film (107)

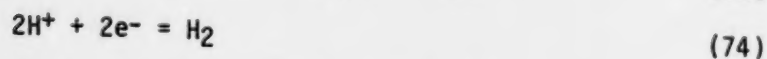
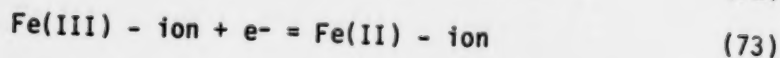
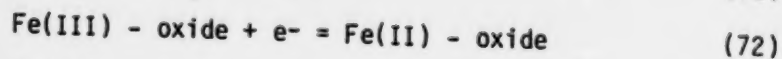
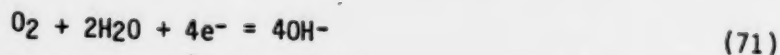
Cohen (107) states that reaction 64 takes place at sites of oxide defects at B and C on the passive metal, thus initiating the corrosion. The possible repair of the passive film is caused by reaction 65. Reactions 66 and 67 are the key reactions that remove the oxide film at A, the widening of the break at B and creating a crack at site C. Equations 68 and 69 are the cathodic reactions at A that are necessary for the initiation and continuation of the anodic reactions (Eqs. 64 and 65) as summarized by Cohen (107).

Wranglen (110) explained that when a pit forms an oxygen cell, it has just moved from its nucleation stage to that of propagation. The interior of the pit acts as a small anode, while its surrounding area becomes a large cathode. The pitting action continues by an "auto catalytic" or self-generating process, because of the desirable conditions for the continuation of corrosion reactions. He further stated that in pitting of steels, only one anodic reaction occurs (Eq. 70) as opposed to several cathodic reactions (Eq. 71-74).

Anodic reaction:



Cathodic reactions:



According to Wranglen (110), reactions 71 and 72 take place outside the pit, while reaction 73 occurs at the mouth of the pit. The evolution of hydrogen (Eq. 74) takes place inside the pit.

The autocatalytic nature of pit propagation and some of the important reactions necessary for the growth of the pit are presented in Figure 47. Pit growth is assisted by a series of oxidation, reduction, hydrolysis, ion migration, diffusion and precipitation reactions that take place both inside and outside the pit.

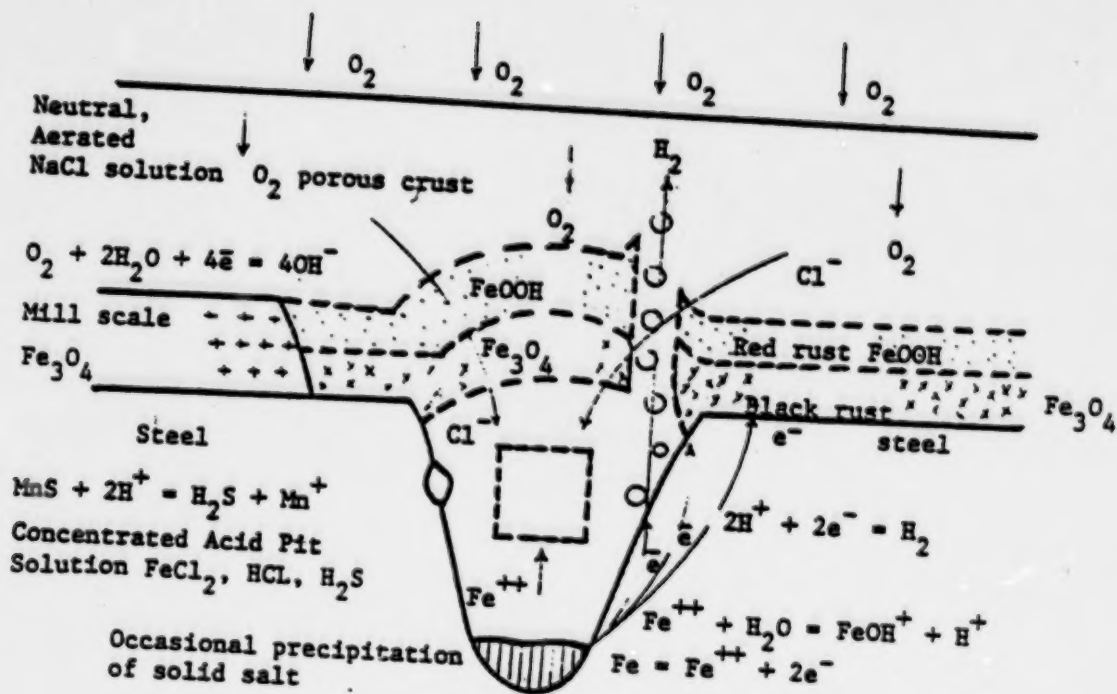
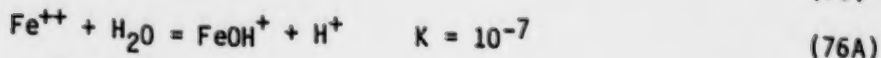
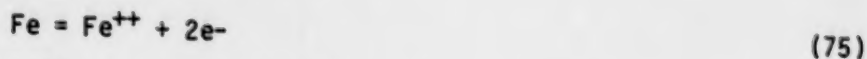


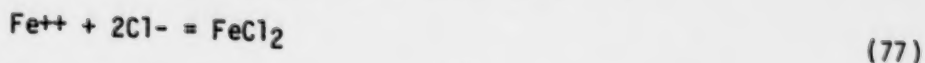
Figure 47. Autocatalytic Nature of Pitting Corrosion of Steel in Neutral Aerated Solution Containing Chloride Ions (110).

Some of the common reactions that occur within the pit are presented in Eqs. 75-80 as described by Wranglen (110). These reactions include the dissolution of iron from the inner walls and bottom of the pit (Eq. 75), the hydrolysis of Fe^{++} ions that generate H^+ ions and results in lowering the pH within the pit (Eq. 76).

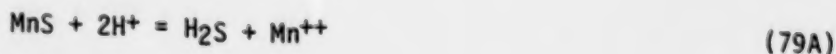


$$\frac{[\text{FeOH}^+]}{[\text{Fe}^{++}]} = 10^{\text{pH} - 7} \quad (76B)$$

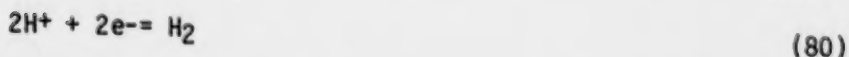
Other reactions that occur within the pit are the enrichment of the pit solution with aggressive anions such as Cl^- (Eq. 77), and SO_4^{--} (Eq. 78) by diffusion, resulting in formation of soluble salts.



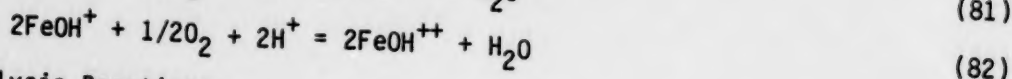
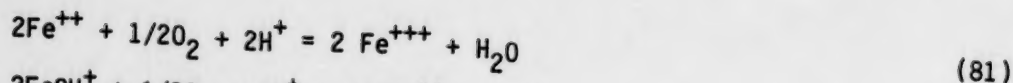
The reactions within the pit are aided by the production of H_2S from the dissolution of sulfide inclusion (Eq. 79) and the evolution of hydrogen gas (Eq. 80).



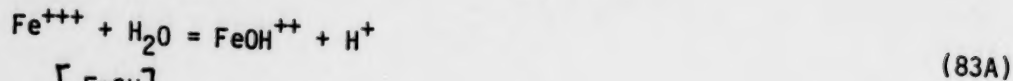
$$\log \text{H}_2\text{S} = 3 - 2 \text{ pH} \quad (79B)$$



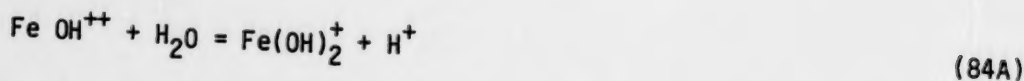
The chemical reactions that occur at the mouth of the pit are shown in Eqs. 81-86. Three types of reactions are prevalent, including the oxidation reactions of Fe^{++} ions (Eq. 81) and FeOH^+ (Eq. 82) by dissolved oxygen; the hydrolysis reactions of Fe^{+++} (Eq. 83) and FeOH^{++} ions (Eq. 84) and the precipitation reactions of magnetite of black rust (Eq. 85) and red rust (Eq. 86) as suggested by Wranglen (110).



Hydrolysis Reactions:

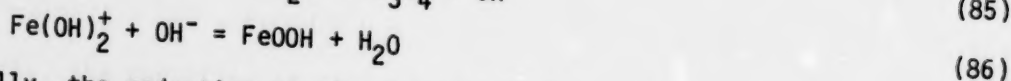
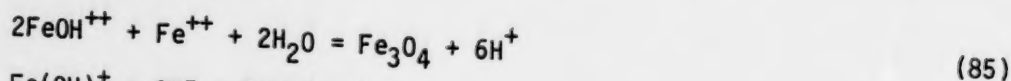


$$\log \frac{[\text{FeOH}]}{[\text{Fe}^{+++}]} = \text{pH} - 3.5 \quad (83\text{B})$$

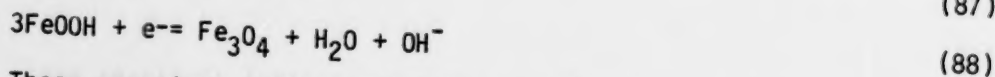
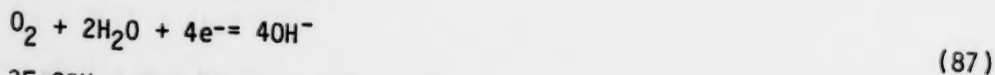


$$\log \frac{[\text{Fe}(\text{OH})_2^+]}{[\text{FeOH}^{++}]} = \text{pH} - 3.5 \quad (84\text{B})$$

Precipitation reactions:



Finally, the reduction of dissolved oxygen (eq. 87) and rust (Eq. 88) both take place outside the pit.



These reactions indicate that the conditions inside and outside of the pit differ in many aspects. For example, reducing conditions such as the presence of low dissolved oxygen, high acidity or low pH, high concentrations of aggressive ions and high electrical conductivity prevail inside the pit, all of which promote the dissolution of the metal (110). The conditions outside the pit are generally oxidizing, with high dissolved oxygen content and are slightly alkaline which favors passivation. The oxidizing and reducing conditions are further aided by the growth of

hydrated tubercles deposited at the mouth of the pit that hinder the free mixing of the pit solution with the bulk electrolyte.

Statistical Evaluation

Since corrosion of metals is affected by many factors, extreme caution should be exercised in reporting and interpreting those results that are based on a limited number of tests. To verify if the rates of corrosion, as affected by different variables, were statistically different from each other, a number of tests were replicated twelve times using Water G (Table 22). The average, the minimum and the maximum rates of corrosion of mild steel as determined by both weight loss and Corrator probes are shown in Tables 25 and 26 respectively. Corrosion data presented in both tables were derived from jar experiments conducted at pH 8.0 to assess the effects of chlorine and color on the corrosion of mild steel. Chlorine concentrations were set at 0.0 and 1.0 mg/l while color concentrations were raised from 0 to 15 Platinum color units (pcu). Corrosion rates were determined after thru exposure periods: 4, 11, and 18 days. In both sets of corrosion data, wide ranges of corrosion rates were found at all immersion time intervals, as indicated by the minimum and maximum values.

Table 25. The Average, Minimum and Maximum Rates of Corrosion of Mild Steel by Weight Loss, pH 8.00

Set No.	Chlorine (mg/l)	Color* (pcu)	Corrosion Rate, mpy								
			4 days			11 days			18 days		
			Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.
1	0.0	0	12.2	8.0	17.0	9.5	7.0	13.0	11.6	4.0	18.0
2	1.0	15	16.4	9.0	26.0	17.9	6.0	32.0	21.8	12.0	47.0
3	1.0	0	14.7	11.0	21.0	17.2	9.0	26.0	21.7	7.0	36.0
4	0.0	15	12.0	10.0	15.0	9.1	6.0	11.0	9.7	6.0	13.0

* Standard Platinum Cobalt units, tests run with 12 replicates.

The averages are plotted in Figures 48 and 49. The following statistics were calculated for the 18-day exposure tests for both Corrator

and weight loss data. The average rates of corrosion, $\bar{x}$ were calculated to determine the central tendency of the data.

The minimum and maximum rates of corrosion were included in Tables 25 and 26 to indicate the dispersion or spread of the data. In addition, the standard deviation, S and the 95% confidence interval CI were also calculated for the data. The computations of the standard deviation and the 95% confidence interval were based on the book of Steele and Torrie (113).

Inspection of the average corrosion rates after the indicated time intervals indicate that corrosion rates of mild steel increased in the presence of chlorine and decreased in the presence of color. For instance, after 4 days, the weight loss measurements showed an increase from 10.1 mpy to 10.6 mpy due to chlorine. On the other hand, corrosion rate was reduced from 10.1 mpy to 8.5 mpy after the same time interval. From electrokinetic measurements, the corresponding changes in corrosion rates are 12.2 mpy to 14.7 mpy due to chlorine and 12.2 mpy to 12.0 mpy due to color. More significant differences can be noted in the values for the two longer immersion periods irrespective of the method employed in determining corrosion rates.

When both chlorine and color were added to the water samples, the average corrosion rates increased relative to those from the samples without chlorine and color. It somehow indicates that the corrosion-promoting effect of chloride predominates over the inhibitory effect of color. Whether the observed effect is crucially influenced by some solution factors is still an open question. More studies will be needed to understand better this phenomenon.

Table 26. Average, Minimum and Maximum Rates of Corrosion of Mild Steel by Corrator Probes, pH 8.00

Set No.	Chlorine (mg/l)	Color (pcu)	Corrosion Rate, mpy								
			4 days			11 days			18 days		
			Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.
1	0.0	0	10.1	5.9	10.4	8.8	6.4	10.0	9.2	5.9	13.2
2	1.0	15	12.5	1.6	17.4	14.8	4.8	20.7	16.0	4.4	24.2
3	1.0	0	10.6	0.8	14.9	12.4	0.9	15.9	13.3	1.4	23.5
4	0.0	15	8.5	4.0	12.1	9.1	4.1	12.7	9.5	3.6	12.7

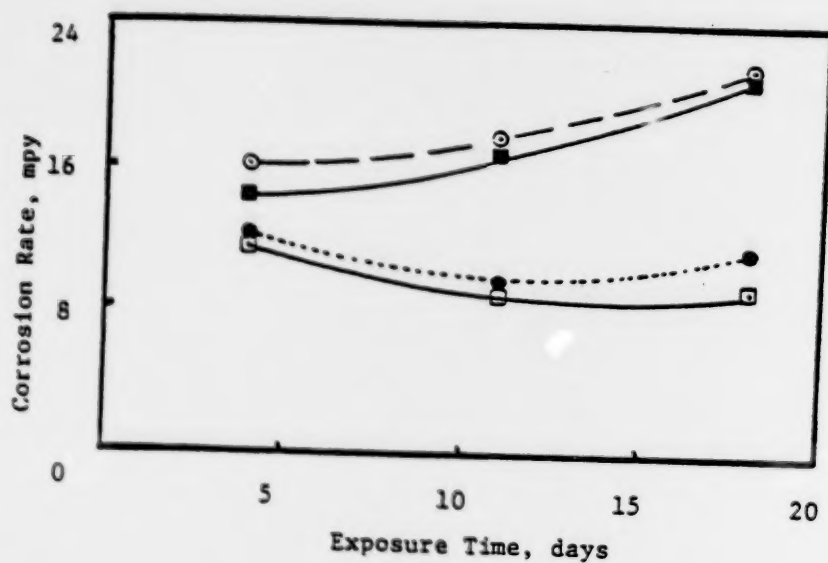


Figure 48. Average Rate of Corrosion of Mild Steel as Determined by the Weight Loss Method pH = 8.00.

- ● No Chlorine or Color
- ○ 1.00 mg/l Chlorine and 15 pcu color
- □ 15 pcu color
- ■ 1.00 mg/l chlorine

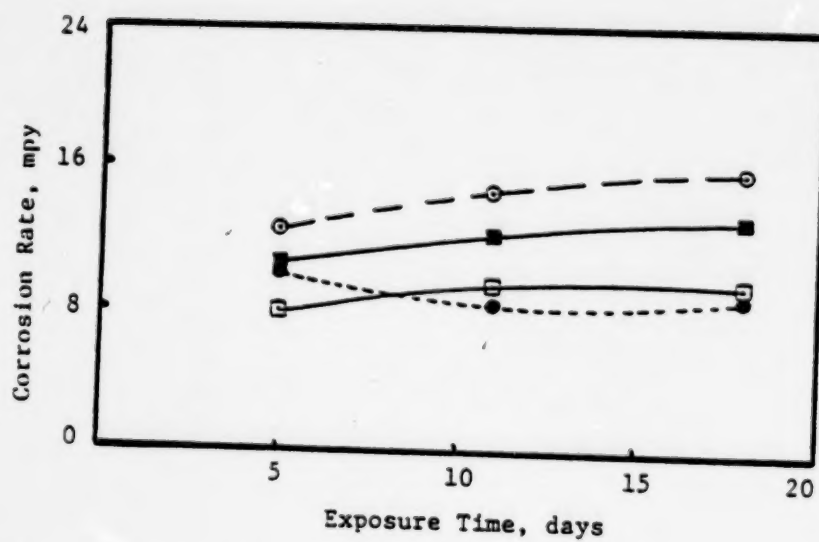


Figure 49. Average Rate of Corrosion of Mild Steel by Corrator Probes, pH 8.00.

- ● No Chlorine or Color
- ○ 1.00 mg/l Chlorine and 15 pcu color
- □ 15 pcu color
- ■ 1.00 mg/l chlorine

The average values of the corrosion rate data of Tables 25 and 26 for the 18-days exposure period were compared to each other using both analysis of variance (ANOVA) and the student t-test. In order to find out if the rates of corrosion as determined by weight loss and Corrator methods were statistically different, the corresponding average values were also compared.

Some of the statistical results are presented in Table 27. Both the analysis of variance and the t statistic revealed a highly significant difference among some of the four sets of tests when a comparison of their means was made.

Table 27. Statistical Results of the Corrosion Rates of Mild Steel, 18-day Exposure

No.	Cl ₂	Color*	Corrosion Rate, mpy					
			Weight Loss			Corrator		
			$\bar{X}$	S	95% CI	$\bar{X}$	S	95% CI
1	0	0	11.6	4.2	9.1-14.1	9.2	2.2	7.8-10.6
2	1.0	15	21.8	9.7	15.6-28.0	16.0	6.7	11.8-20.2
3	1.0	0	21.7	9.5	15.7-27.8	13.3	7.2	9.5-18.7
4	0	15	9.7	2.0	8.4-11.0	9.5	2.5	7.9-11.1

*Chlorine in mg/l and color in pcu's.

In the weight loss data, no difference in corrosion rate was detected at the 95% level of confidence between sets 1 and 4, and sets 2 and 3. This means that natural color did not influence the rates of corrosion. The difference in rates of corrosion was found to be highly significant (99% level of confidence) between sets 1 and 2; sets 1 and 3; sets 2 and 4 and sets 3 and 4, meaning that chlorine accelerated the rate of corrosion of steel.

In comparison to the Corrator data, a highly significant difference (99% confidence level) was observed between sets 1 and 2; and sets 2 and 4. A significant difference (95% confidence level) was seen between sets 1 and 3, and sets 3 and 4. No difference was detected between sets 1 and 4 and sets 2 and 3.

When the rates of corrosion obtained by the weight loss method were

compared with those measured by the Corrator, on a one-to-one basis, no statistically significant difference was detected except in sets 3 which were different at 95% level of confidence. Although the results of the Corrator measurements were numerically lower than the rates measured by weight loss, the statistical analysis of the data indicates a correlation between these two measurement techniques.

Galvanized Steel

To protect iron or steel from extensive corrosion damage, zinc is plated on iron or steel pipes to produce galvanized steel. Since this type of pipe was introduced to the water industry, the presence of zinc in water supplies has been observed (114) and studies of the corrosion of galvanized iron (115-117) have received attention. Fundamental investigation of the properties of zinc, such as its electrochemical behavior (118) and the natural pitting of its crystals (119), as well as the effect of anions on the corrosive behavior (117), have been conducted. To gain additional knowledge on the corrosive reaction of zinc in potable water systems, experiments in jar systems and loop studies were conducted.

Corrosive Behavior of Galvanized Steel in Five Waters of Different Saturation Indices

Five waters with saturation indices ranging from -2.12 to +1.90 were evaluated for their corrosivity towards galvanized steel using jar tests. The results are shown in Figure 50 which illustrates the corrosion versus time curves for galvanized steel in the test waters with DO = 5.0±0.2 mg/l. Water "e" (SI = -2.12) and "g" (SI = -1.06) were found to be the most corrosive of the waters. The corrosion rates in waters "o" (SI = +1.03) and "q" (SI = +1.90) were comparable within the limit of experimental error and were the lowest. The corrosion rates in all waters decreased as the exposure times were increased, similar to the corrosion versus time curves obtained for mild steel in the same jar systems. Corrosion was usually faster during the first few days because the tendency of zinc ions to be removed from the metal surface is thermodynamically more favored when the solution had no or a very low concentration of zinc ions. In addition, the surface of the galvanized steel initially was totally exposed to the solution so that at even a constant corrosion rate there was more metal exposed than when the metal was partially covered by a coating of corrosion products. As soon as the solution became enriched with zinc ions and the metal surface exposed became less the corrosion was suppressed. This could account for the lower corrosion rates observed after 10 or 20 days.

The changes in zinc concentration during corrosion are presented in Figure 51. The amount of dissolved zinc generally increased after 3 and 5 days for all the waters used. In waters "e" and "g", the zinc

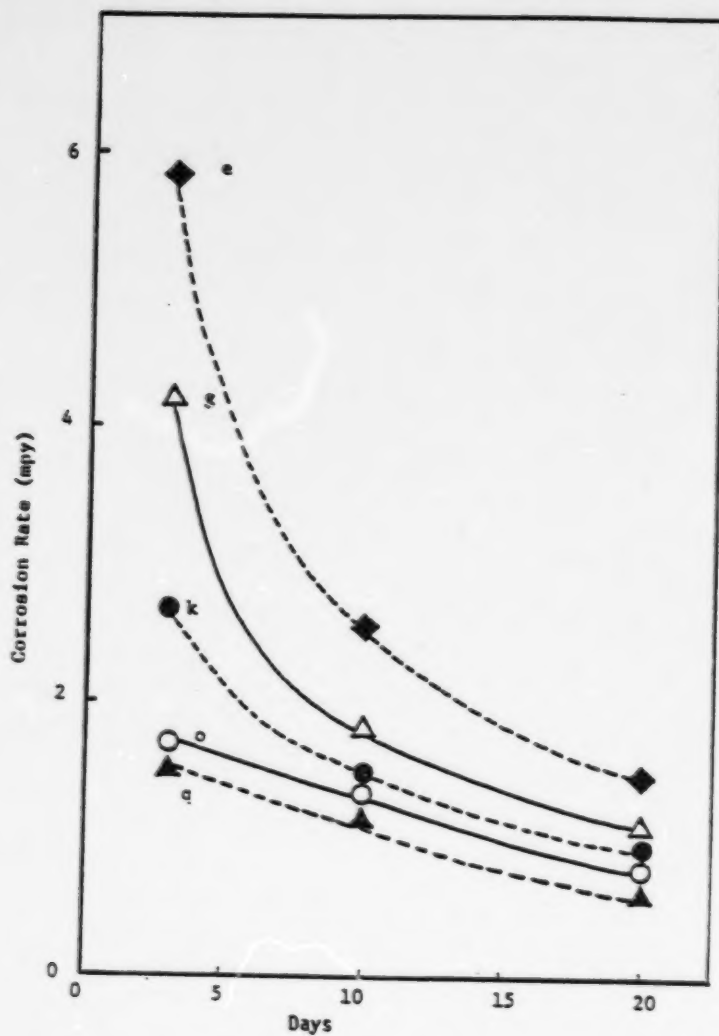


Figure 50. Corrosion Rate versus Time Curves for Galvanized Steel in Jar Systems with Five waters of Different Saturation Indices. The Waters Used were "e" (SI = -1.06), "k" (SI = +0.07), "o" (SI = +1.03) and "q" (SI = +1.90).

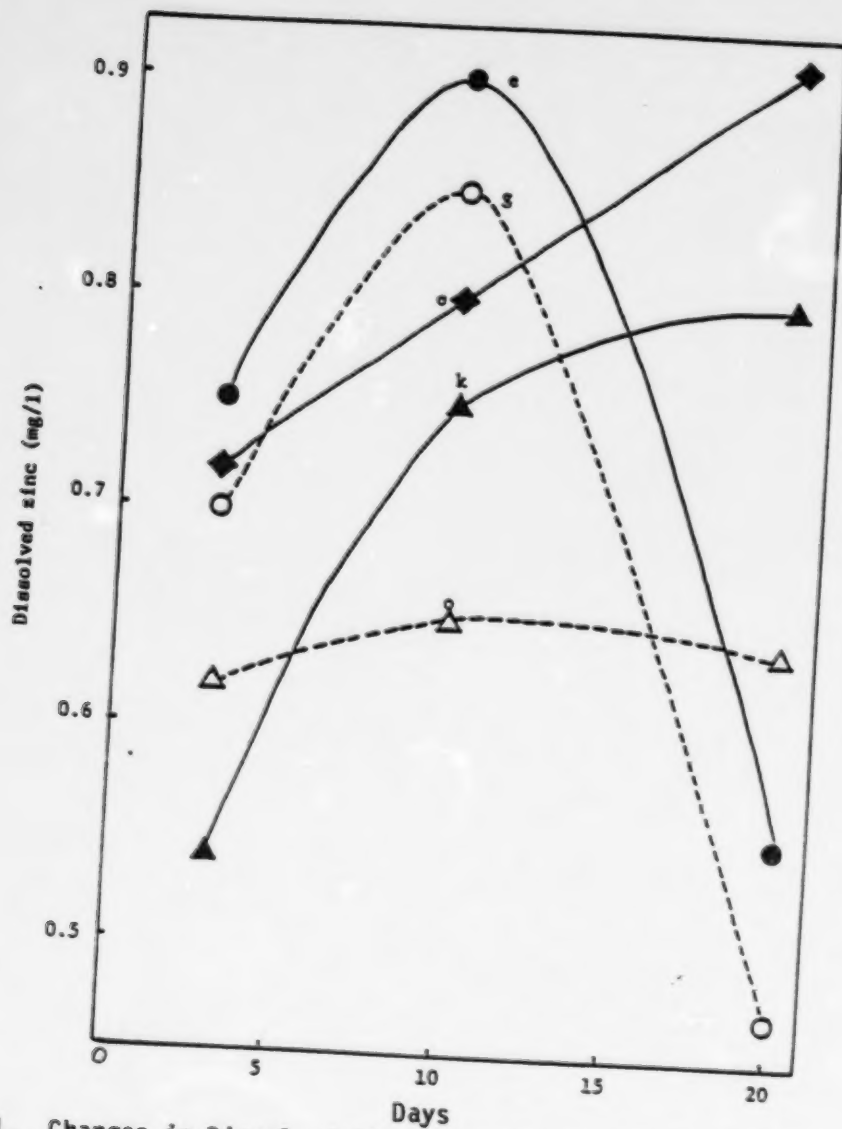


Figure 51. Changes in Dissolved Zinc Concentration with Time During the Jar Corrosion Tests Involving Five Waters of Different Saturation Indices.

concentration went down abruptly at the 20th day, which indicated consumption of aqueous zinc by formation of zinc oxide or hydroxide or other zinc compounds. The dissolved zinc-time profile for waters "q" and "k" indicated a continuous increase in zinc concentration which could imply two things. First, the concentration of soluble zinc that could exist in equilibrium with its salts or oxides had not been reached. The precipitation of such compounds would have been affected by the ionic composition of the solution. Secondly, it was possible that the metal was still releasing Zn^{+2} , which could form soluble complexes with anions, such as OH^- or CO_3^{--} . On the other hand, dissolved zinc in water "o" did not exhibit as much variation with time which probably reflected that the equilibrium concentration became stable.

Effect of pH

The corrosion of galvanized steel in deionized and Gainesville water at different pH values is shown in Figure 52. The pH of the water had been adjusted by titration with 0.01 N HCl or 0.02 N NaOH to the desired value. Corrosion rates in deionized water were faster than those in Gainesville water at all pH levels. This was similar to the results for the corrosion of mild steel. The greater extent of corrosion observed in deionized water compared to Gainesville water could be due to two important factors, namely, the very low alkalinity and the high dissolving tendency for zinc in deionized water. In other words, the absence of the corrosion inhibiting effect of alkalinity, coupled with a favorable thermodynamic potential for zinc to enter into solution, caused more rapid corrosive attacks on galvanized steel in deionized water. In both waters, however, higher corrosion rates were observed at acidic pH values, 5.0 to 6.0, while the lowest rate was at pH 7.0. The corrosion curve tended to increase at around pH 8.0 where the buffer capacity of Gainesville water was at a minimum, assuming no significant changes in alkalinity took place. Under alkaline conditions, corrosion rates in both waters were lower which could be due to a large extent to the passivation of zinc via formation of zinc oxide or hydroxide that acted as a protective film against corrosion. Because of the oxidation or hydroxylation of zinc ions at higher pH, the amount of dissolved zinc would be expected to decrease. Thus, at pH 8.5 and pH 9.0, the zinc concentration was lower compared to that at the other pH levels as shown in Figure 52. The highest concentration was at pH 5.0 for both waters, not only because the corrosion rate was maximum at this pH, but also due to higher solubility of the compounds comprising the corrosion products at lower pH. It should be noted again that at all pH values, the amount of dissolved zinc was higher in deionized water than in Gainesville water.

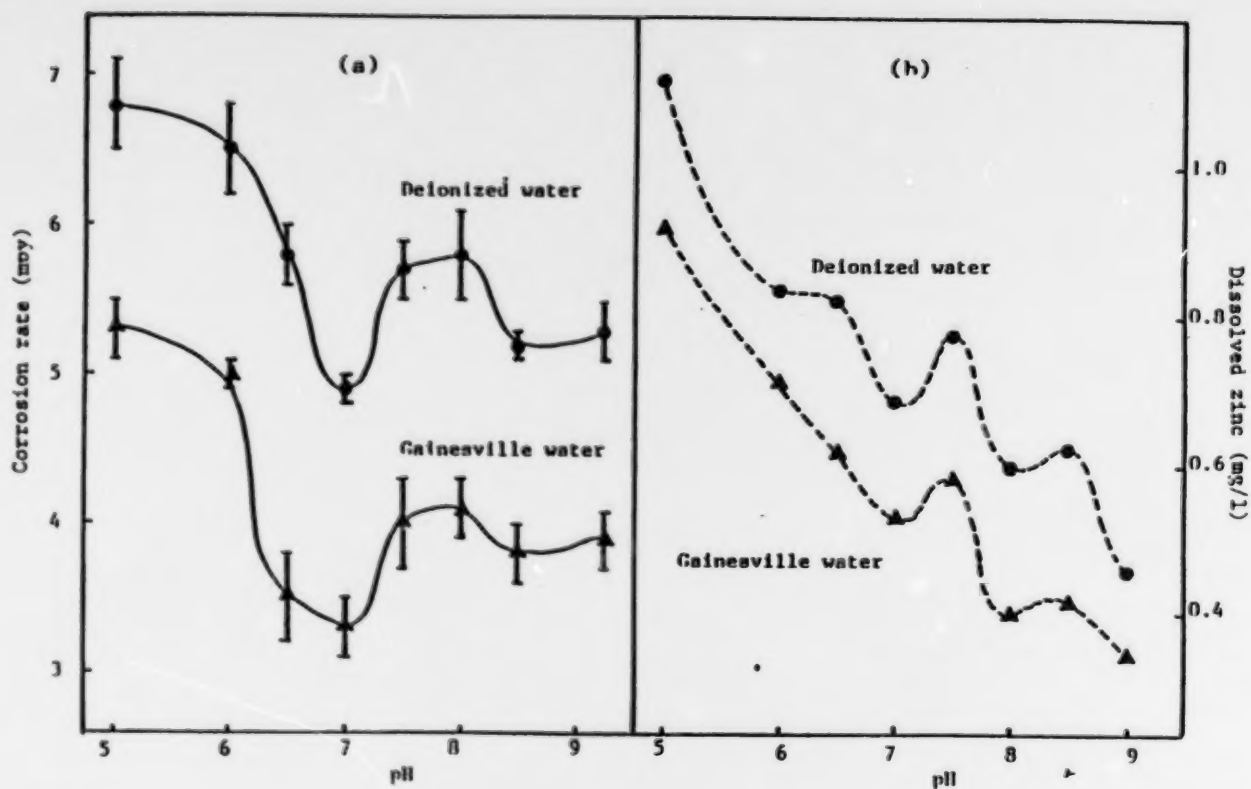


Figure 52. Corrosion Rate - pH (a) and Dissolved Zinc - pH (b) Profiles from Five-Day Corrosion Measurements in Jar Tests Using Galvanized Steel.

Influence of Dissolved Oxygen

The effect of DO on the corrosion of galvanized steel was evaluated using jar tests at two DO concentrations, 5.0 and 9.0 mg/L. Table 28 shows that the corrosion rates in waters with DO of 9.0 ± 0.2 mg/L were always

Table 28. Corrosion of Galvanized Steel After 5 Days in Five Waters with Different Saturation Indices as Affected by the Level of Dissolved Oxygen (DO)*

Water	SI	Corrosion Rate (mpy)	
		DO = 9.0 ± 0.2 ppm	DO = 5.0 ± 0.2 ppm
e	-2.12	4.8 ± 0.6	3.5 ± 0.5
g	-1.06	3.9 ± 0.8	2.6 ± 0.4
k	+0.07	4.5 ± 0.7	2.5 ± 0.6
o	+1.03	4.0 ± 0.4	1.6 ± 0.4
q	+1.90	1.8 ± 0.3	1.4 ± 0.4

*Each corrosion rate reported as a mean value of three measurements. Mean corrosion rate $\pm$ one standard error.

higher than those in waters with lower DO concentrations (5.0 ± 0.2 mg/L). The corrosion rates in waters with DO of 5.0 ± 0.2 mg/L varied from 1.4 to 3.5 mils/year while the rates in most O_2 -saturated systems ranged from 1.8 to 4.8. It was found that generally corrosion at DO = 5.0 ± 0.2 mg/L was much faster in waters with increasingly negative saturation index with the exception of water "k". The lower corrosion rate observed in waters with higher positive saturation index could be attributed to the greater tendency to form protective calcite deposits on the metal surface. Furthermore, with increasing alkalinity, the formation of smithsonite ($ZnCO_3$) or hydrozincite [$Zn_5(CO_3)_2(OH)_6$] would be favored, which could coat the metal surface and thus suppress corrosion. In aqueous systems with higher oxygen concentration, two competing effects could be possible. With increase in oxygen, the corrosion rate could be enhanced as a result of a faster reaction of oxygen with zinc ions released from the corroding galvanized steel. However, if the oxides or hydroxides of zinc were formed fast enough and adhered to the metal surface, the corrosion rate would be retarded. The adherent oxide film would passivate the metal under this condition. Hence, it does not necessarily follow that increasing oxygen would always increase the corrosion rate.

Effect of Water Quality

The rates of corrosion of galvanized steel specimens in aerated waters of different chemical composition (Table 29) are illustrated in Figure 53. The effects of both water composition and time, on the rate of corrosion of the zinc coating are shown. The rate of dissolution of the zinc was greatly affected by the water quality which is illustrated by the fact that it was the highest in Water G (low mineral content) and the lowest in Water I (high mineral content).

Galvanized steel in comparison to mild steel appears to be more sensitive to the changes in the chemical composition of the waters (Figure 53). The difference in the rates of corrosion can be attributed to the formation of basic zinc carbonate on the surface of the zinc. In hard waters, the aggressive action of water on the zinc coating is hampered due to the potential of the water to form such films on the corroding metal surface. Visual inspection of the samples revealed that the corrosion product on the zinc surface was more firmly attached to the metal in hard waters than in soft waters.

Rice (120) found similar results and reported that high bicarbonate hardness resulted in better protection of the galvanized steel piping. Although galvanized steel specimens were exposed to solutions without any surface preparation (such as polishing with abrasive paper), the resulting data indicate that the rates of corrosion were generally not influenced by the original quality of the zinc coating. Only two galvanized steel specimens, out of a total of 336 that were exposed in a single set of experiments, showed some rusting of the steel at selected points after 45 days of exposure.

Effect of Chlorine Residual

The effect of chlorine residual on the rate of corrosion of galvanized steel in aerated solutions is shown in Figure 54. The presence of a chlorine residual greatly increased the rate of corrosion. The rates of corrosion were higher in all chlorinated systems compared to those containing no chlorine. A similar effect was observed in deaerated test solutions, i.e. the rates of corrosion of galvanized steel were higher in solutions containing chlorine, though the difference was not as pronounced as in aerated systems.

Chlorine enhances corrosion of metals both by increasing the redox potential of the solution and by its reduction to chloride ion. Dissolved oxygen and chlorine were found to have an additive positive effect.

Table 29. Corrosion Rates of Galvanized Steel in Waters G, H, and I.

Water*	Color (pcu)	Chlorine (mg/l)	Corrosion Rate, mpy			
			10 days	20 days	30 days	45 days
G -O	0	0	2.36	2.23	2.20	2.25
G -O	0	1	3.07	2.91	2.85	2.90
G -O	10	1	2.86	2.68	2.75	2.75
G -O	10	0	1.58	1.72	1.60	1.80
G -N	0	0	0.46	0.33	0.45	0.50
G -N	0	1	0.61	0.67	0.58	0.80
G -N	10	1	0.44	0.37	0.40	0.60
G -N	10	0	0.26	0.21	0.25	0.30
H -O	0	0	1.24	1.11	1.15	1.25
H -O	0	1	2.25	2.08	1.90	2.10
H -O	10	1	1.79	1.50	1.65	1.60
H -O	10	0	0.98	0.77	0.85	1.02
H -N	0	0	0.28	0.31	0.35	0.35
H -N	0	1	0.40	0.43	0.45	0.50
H -N	10	1	0.35	0.40	0.40	0.30
H -N	10	0	0.28	0.18	0.15	0.20
I -O	0	0	0.59	0.55	0.60	0.65
I -O	0	1	1.61	1.35	1.40	1.50
I -O	10	1	1.04	1.23	1.10	1.35
I -O	10	0	0.30	0.35	0.40	0.50
I -N	0	0	0.30	0.30	0.35	0.40
I -N	0	1	0.45	0.35	0.40	0.45
I -N	10	1	0.40	0.42	0.40	0.45
I -N	10	0	0.10	0.15	0.15	0.20

*Letters G, H, and I refer to the types of Water (Table 22); letter O indicates aeration and letter N shows no aeration.

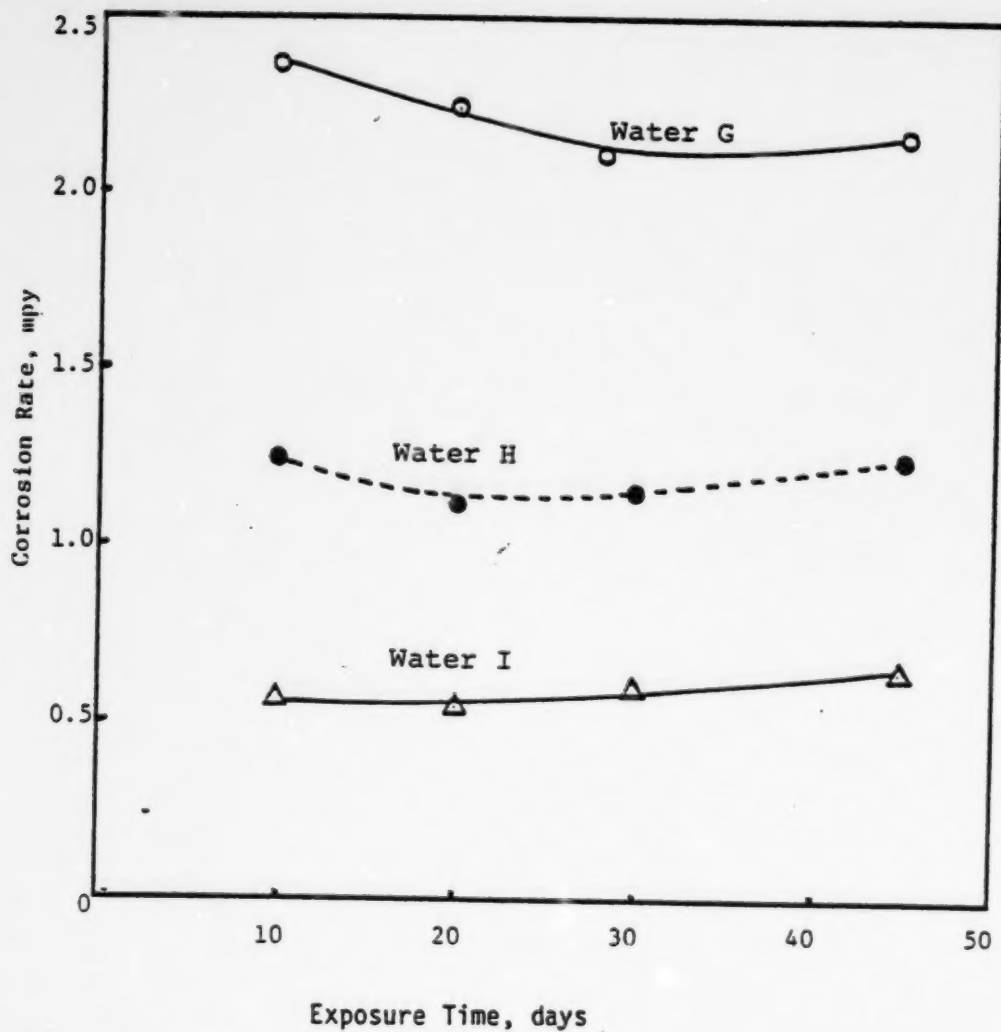


Figure. 53. Rate of Corrosion of Galvanized Steel as Affected by Water Quality.

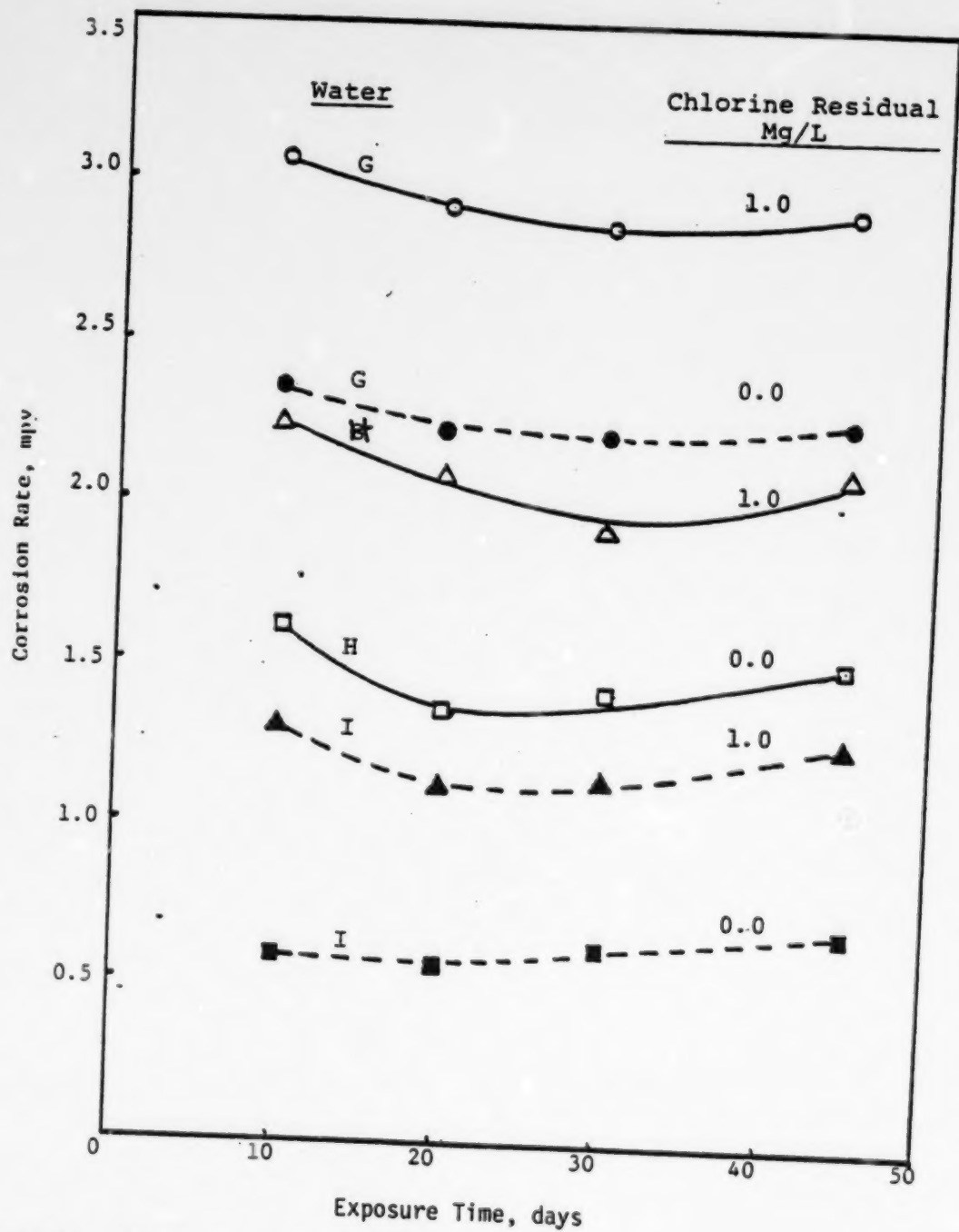


Figure 54. Effect of Chlorine Residual on the Rate of Corrosion of Galvanized Steel in Aerated Solutions.

Natural Color

The addition of natural color to water at 10 pcu's reduced the rates of corrosion of galvanized steel in all test waters (Figure 55). The reduction in the rates of corrosion was the highest in Water G than in either Waters H or I. Rice (120) reported that the presence of natural color inhibited the corrosion of galvanized steel when used for conveying natural or zeolite-softened water. The addition of 10 pcu's of natural color also had a negative effect on the rate of corrosion of galvanized steel in chlorinated solutions. The reductions in the rates of corrosion, however, were not as pronounced as in solutions containing no chlorine.

Effect of Specific Ions

The effects of chloride, sulfate and bicarbonate ions on the rates of corrosion of galvanized steel in aerated solutions are summarized in Figure 56. The rates of corrosion of galvanized steel increased slightly with increasing concentrations of both chloride and sulfate ions and decreased with increasing concentrations of bicarbonate ions. Bicarbonate ions had an inhibitory effect on the rate of corrosion of galvanized steel, even in the absence of any calcium salts. The reduction in the rate of corrosion of galvanized steel by bicarbonate ions was probably due to the buffering effect of carbonic species in water. Sulfate ions were found to be more aggressive to galvanized steel than were chloride ions at similar concentrations. The rates of corrosion of galvanized steel were higher in chloride and sulfate solutions, because both chloride and sulfate ions are conjugate bases of strong acids, that form soluble compounds in solutions.

The data presented in Figure 56 were obtained from solutions containing only one cation and one anion. The results of tests containing either chloride or sulfate ions as well as Ca^{++} , Mg^{++} and Na^{+} ions are illustrated in Figure 57. The rates of corrosion, again were found to be higher in sulfate solutions than in chloride solutions. The combination of both chloride and sulfate ions in equal amounts in a single solution, gave intermediate corrosion rate values. The variation of corrosion rate of galvanized steel with respect to the ratio of $(\text{Cl}^{-} + \text{SO}_4^{--}) / \text{Alkalinity}$, (ratio in meq.) is shown in Figure 58. The results indicate that the rate of corrosion increases with increasing $(\text{Cl}^{-} + \text{SO}_4^{--}) / (\text{Alkalinity})$ ratio.

According to Evans (121), as noted by Rice (120), the holidays and imperfections in zinc coatings are covered by the deposition of high bicarbonate hardness that protects both zinc and steel from corrosion. Hoxeng and Prutton, (118) in a study of the zinc-steel couple concluded that increasing bicarbonate ions shifted the zinc potential in the anodic direction in aerated solutions. Evans (122) as noted by Hoxeng and Prutton (118) reported that chloride and sulfate ions promote the dissolution of zinc due to the high solubility of zinc chloride and zinc

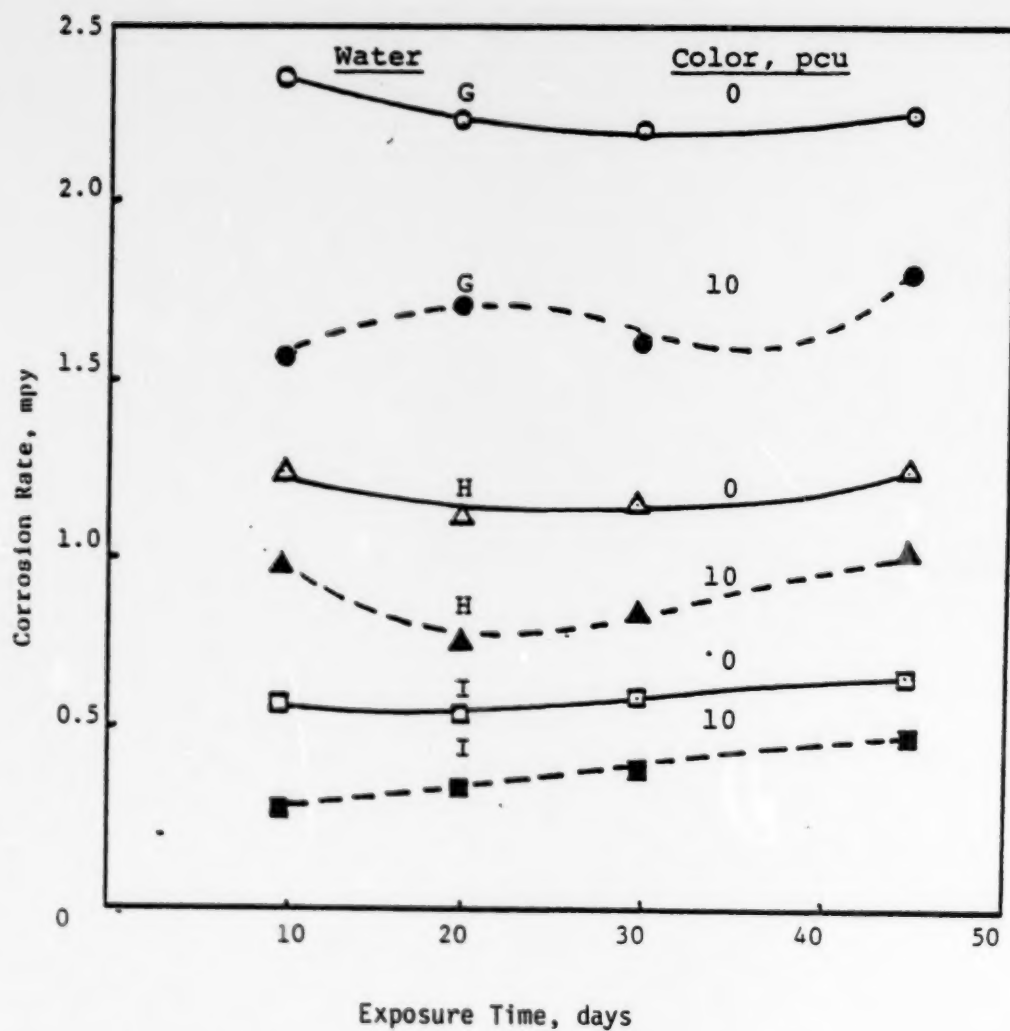


Figure 55. Effect of Color on the Rate of Corrosion of Galvanized Steel in Aerated Solutions.

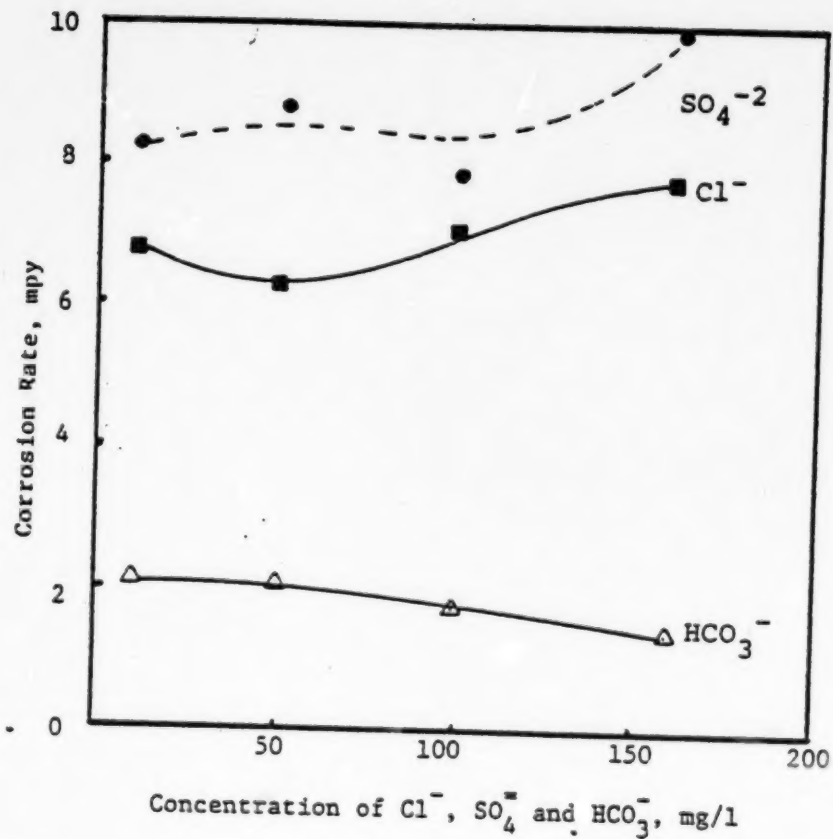


Figure 56. Effect of Chloride, Sulfate and Bicarbonate Ions on the Rate of Corrosion of Galvanized Steel in Aerated Solutions. Salts of Sodium Added. Exposure Time, 14 days.

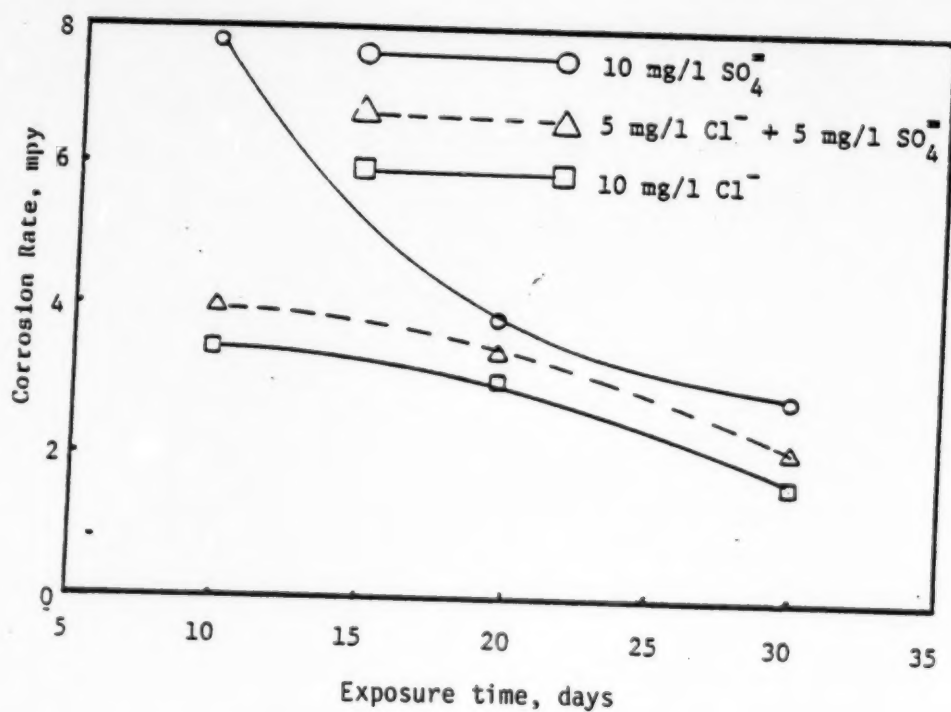


Figure 57. Effect of Chloride and Sulfate on Corrosion of Galvanized Steel in Aerated Solutions Containing Ca^{++} , Mg^{++} , and Na^{++} ions. pH 7.35

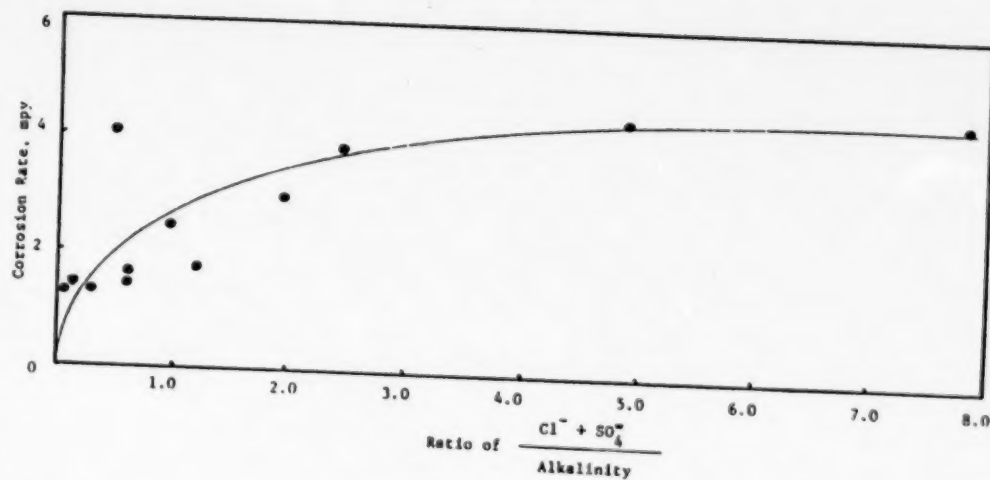


Figure 58. Effect of Ratio of $\frac{Cl^- + SO_4^{2-}}{Alkalinity}$ on the Corrosion of Galvanized Steel.

sulfate products at the anodic sites. Furthermore, chloride and sulfate ions have been shown to penetrate metallic oxide films and thus initiate corrosion (118). Davies and Lotlikar (123) showed that increasing chloride concentration caused pitting of zinc in alkaline solutions, in the pH range 9.2-12.3.

Redox Potential

The redox potential (Table 30) of several corroding galvanized specimens were monitored periodically and the data are summarized in Figure 59. The measured redox potential data are in close agreement with the experimentally determined corrosion rate values. This means that a positive correlation between redox potential and the rate of corrosion of galvanized steel exists. The presence of 1 mg/l of chlorine residual had a profound effect on the redox potential of both aerated and deaerated solutions. The redox potential increased slightly with increasing exposure time, in aerated systems that contained no chlorine, while it decreased slightly in all chlorinated and deaerated systems.

Figure 60 shows the redox potential measured in the study of the E_H -pH diagram for zinc. Most of these redox potentials coincided with the ZnO or $Zn(OH)_2$ stability region under both aerated and deaerated conditions. Only a few redox potential values in aerated solutions occurred in the region of stability of Zn^{++} , implying active oxidation of zinc to zinc ions.

Variation in Water Quality

The changes in the water quality were monitored periodically for both zinc and cadmium pick-up by solution from the exposed galvanized steel specimens (Table 31). The leaching of zinc against time is shown in Figure 61. The concentration of zinc did not vary appreciably after two weeks of exposure time. Most of the zinc was found attached to the corroding surface of the coupons, while some zinc precipitated in the jar as corrosion continued. The concentration of soluble zinc was found to be only 10-20 percent of the total concentration of zinc. No cadmium was detected in any samples.

Table 30. Redox Potential of Galvanized Steel
in Aerated Synthetic Waters.

Water	Chlorine (mg/l)	E h				
		2 days	8 days	21 days	30 days	45 days
G	0.0	523	522	539	546	556
H	0.0	501	506	509	509	514
I	0.0	496	491	505	516	512
G	1.0	908	876	868	862	857
H	1.0	895	888	864	853	846
I	1.0	872	855	831	825	830

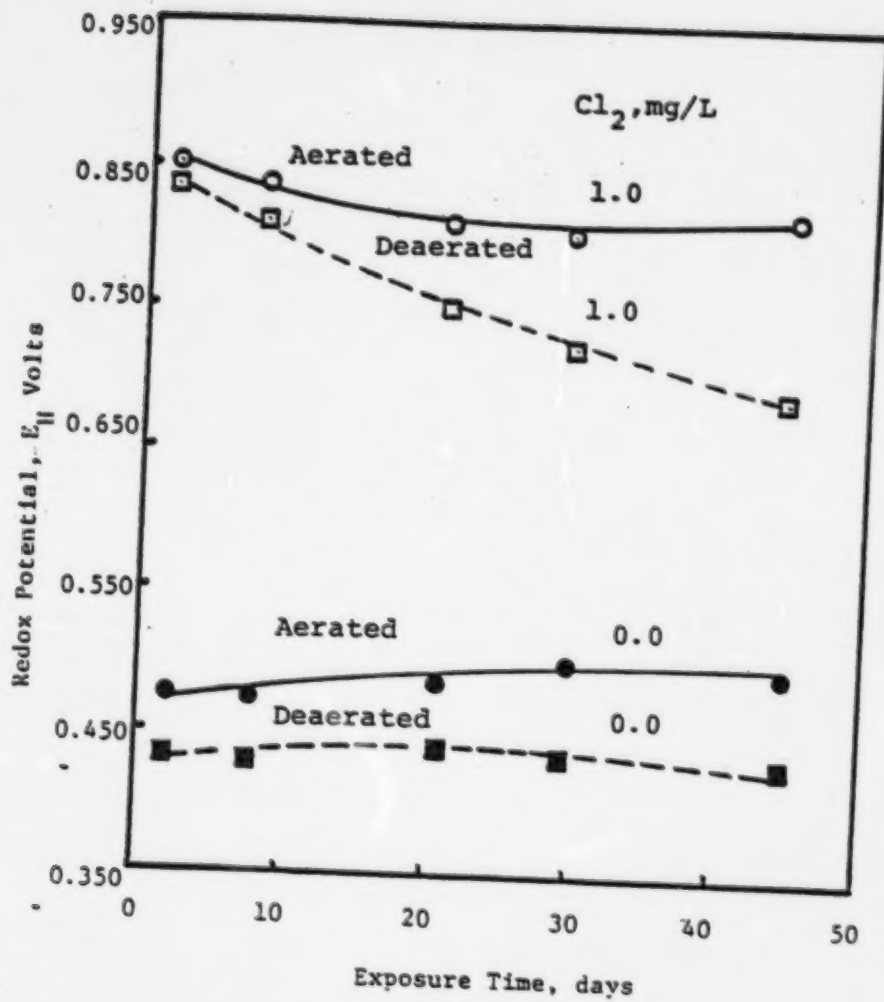


Figure 59. Variation in Redox Potential of Galvanized Steel Immersed in Water I, pH 8.45.

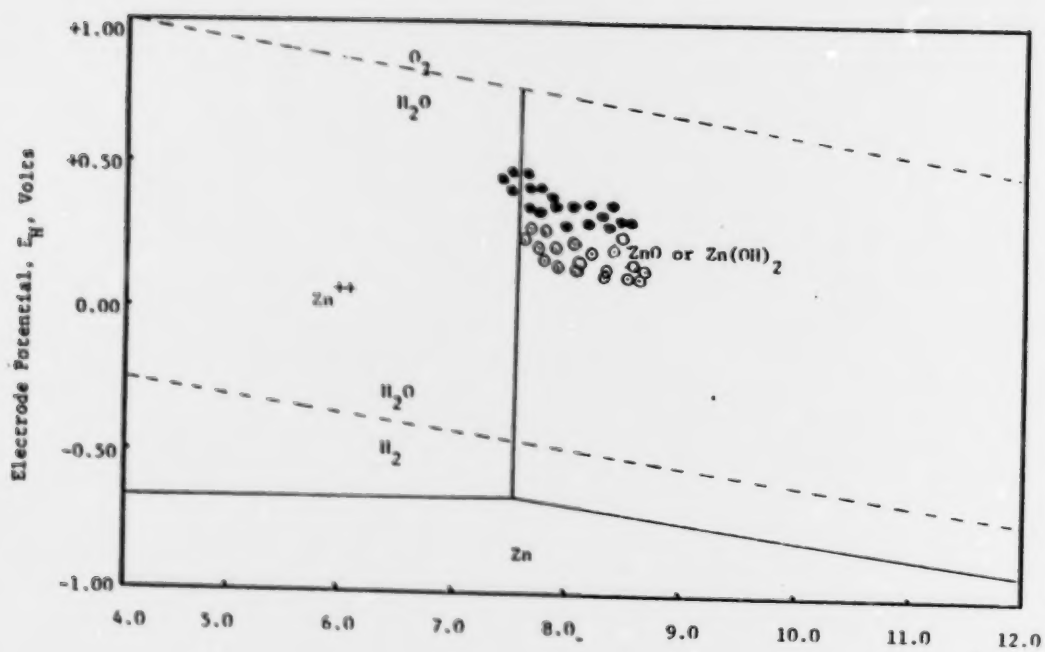


Figure 60. Pourbaix Diagram for 7.6×10^{-5} M Zn in the Presence of 100 mg/l Alkalinity as $CaCO_3$, with Measured E_H Values.

● Aerated

○ Deaerated

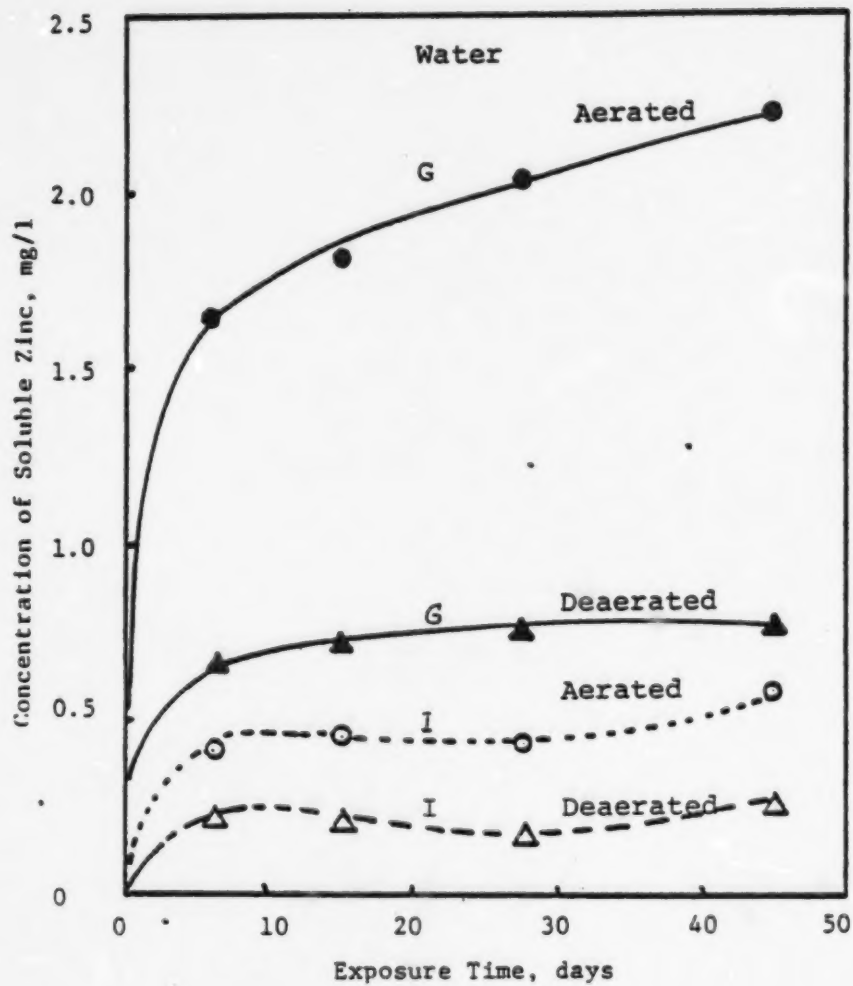


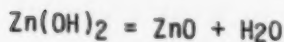
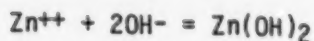
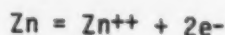
Figure. 61. Leaching of zinc from Galvanized Steel Specimens Exposed to Different Solutions.

Table 31. Concentration of Soluble Zinc
in Synthetic Solutions.

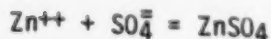
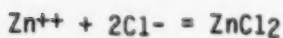
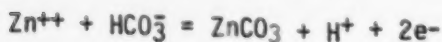
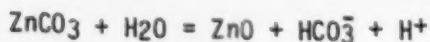
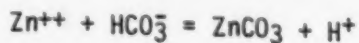
Water	Dissolved Oxygen, Mg/l)	Zinc Concentration, mg/L			
		6 days	15 days	28 days	45 days
G	8.45	1.65	1.82	2.04	2.22
H	8.43	0.84	0.85	0.85	0.92
I	8.45	0.65	0.71	0.75	0.75
G	0.15	0.42	0.45	0.43	0.58
H	0.20	0.28	0.28	0.29	0.38
I	0.18	0.21	0.20	0.18	0.27

The Nature of Corrosion

Corrosion of zinc is governed by many factors. The chemical composition of the solution, pH, chlorine residual, redox potential, dissolved oxygen and color, all affect the rate of corrosion of galvanized steel. Zinc has been shown to be passivated in dilute sodium hydroxide solutions (124) forming a thin (three monolayers) film composed of Zn(OH)_2 or ZnO . The chemical reactions that lead to the passivation of zinc include



When bicarbonate, chloride and sulfate ions are present in a solution, the following chemical reactions take place



Zinc, as compared to iron and copper, has a simple chemistry. The rates of corrosion of zinc were strongly affected by oxygen, chlorine residual color, and alkalinity.

Copper

According to Cohen and Lyman (125), over 6 million miles (7 billion pounds) of copper tube have been used for plumbing in the United States since World War II. This increased use of copper is attributed to its satisfactory performance under normal conditions of exposure. However, copper like any other material of construction is not immune to corrosion. Certain operating conditions and water quality parameters have been found to cause premature failure of copper pipes.

Several experiments were conducted on copper under laboratory conditions to evaluate its rate of corrosion in synthetic solutions of different quality. The test conditions closely matched those of the mild steel experiments, except that longer exposure time was necessary for copper because of lower corrosion rates. A number of tests were also performed under laboratory conditions on an actual water supply from Pinellas County, Florida that had been shown to be corrosive to copper services. The actual water used in the tests had the following chemical composition: pH = 7.78; Ca^{++} = 81 mg/l; Mg^{++} = 8 mg/l; Na^+ = 14 mg/l; Cl^- = 41 mg/l; SO_4^{--} = 17 mg/l and alkalinity = 186 mg/l, expressed as CaCO_3 .

Effect of Water Quality

The rates of corrosion of copper in aerated waters of different chemical composition (Table 32) are presented in Figure 62, from which two conclusions can be drawn: first, that the rate of corrosion of copper decreased almost linearly with exposure time, and second, no real difference in the rate of corrosion of copper can be noted on the basis of the water quality. The type of corrosion observed was general, with no visible pitting. Most of the copper specimens remained bright throughout the exposure period, while a few specimens experienced discoloration and had a brownish appearance. A possible explanation for the absence of pitting in the copper corrosion tests may be the uniformity of the exposed surface of the copper specimens. It has been shown (126) that surface inhomogeneity (mill scale, localized carbon films or irregular oxide films) causes the pitting of copper.

Obrecht and Quill (127-132) in a series of static and dynamic tests on the corrosion of copper concluded that the quality of water alone is not the major factor, but that temperature, velocity, dissolved oxygen, and other operating conditions play important roles in copper dissolution.

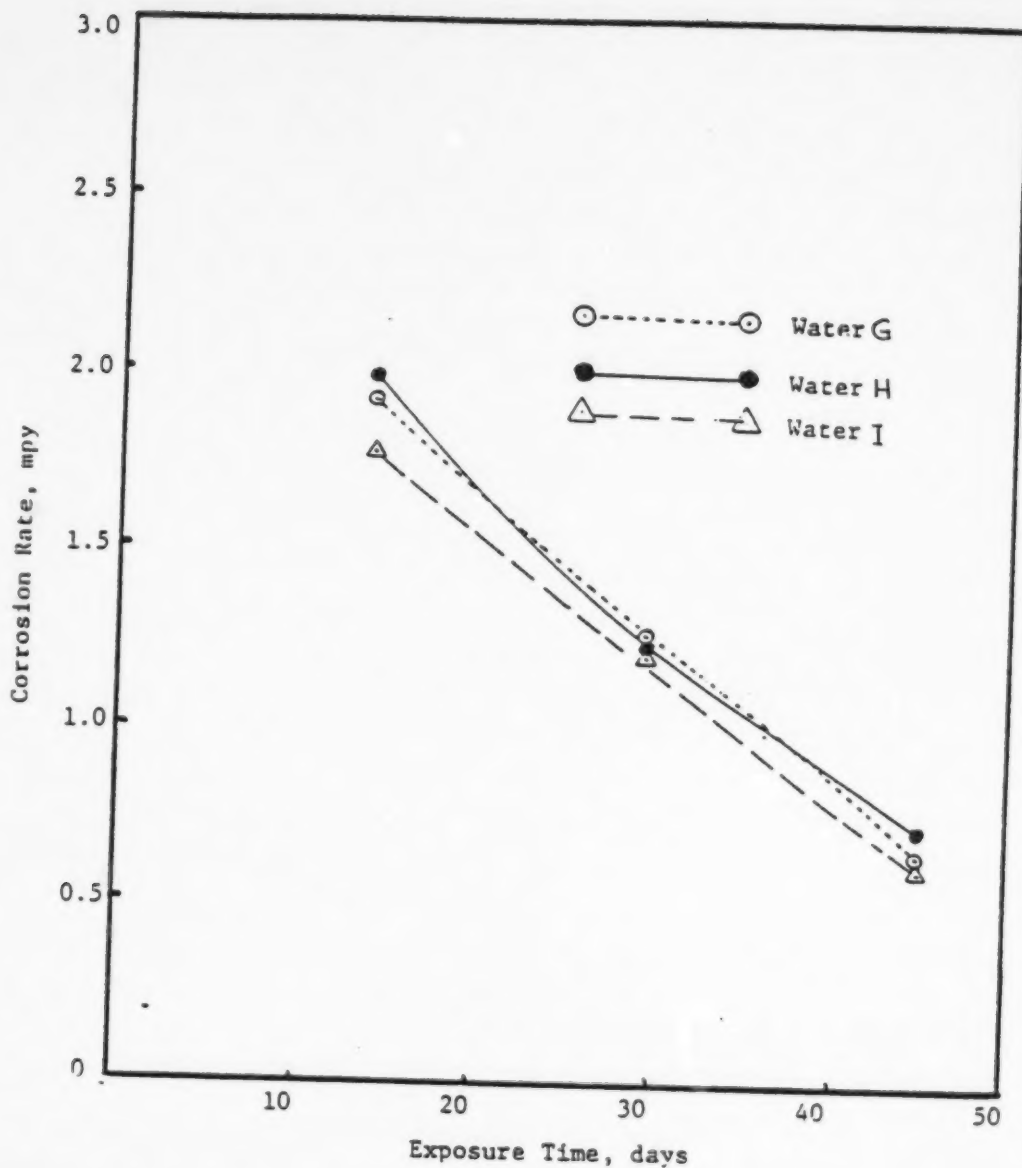


Figure 62. Effect of Water Quality on the Rate of Corrosion of Copper in Aerated Solutions.

Table 32. Rate of Corrosion of Copper in Aerated Solutions,
by Weight Loss Method

Type of Water*	Color (pcu)	Corrosion Rate, mpy		
		15 days	30 days	45 days
G	0	1.91	1.23	0.59
G	15	2.13	1.50	0.60
H	0	1.98	1.22	0.67
H	15	2.75	1.34	0.66
I	0	1.78	1.21	0.58
I	15	1.95	1.14	0.60

*For composition of the type of water, refer to Table 22.

Cole (133) noted the satisfactory use of copper tubes in waters that were similar in chemical composition to those used in this study (Table 22). The rates of corrosion of copper in the tap water in both aerated and deaerated systems are shown in Figures 63 and 64.

The rates of corrosion of copper (Tables 33-34) were found to decrease the increasing time. The rate of dissolution of copper declined at a faster rate in the tap water than in synthetic solutions. This could be attributed to the presence of high calcium and alkalinity in the natural water and the development of a protective calcite coating on the surface of the metal. The instantaneous rate of corrosion of copper (Figure 63) shows a greater scatter in the data, although the general trend is similar to that of the weight loss data.

Effect of pH

The rates of corrosion of copper as determined by the weight loss methods in the tap water, was found to be independent of pH over the range 7.40-8.00. Figure 65 is a plot of these data. No correlation was observed between pH and the instantaneous corrosion rate values.

Newell (134) reported that of the three variables, pH, temperature and velocity, the effect of pH on the rate of corrosion of copper was the lowest of the three variables, and also noted that the rate of corrosion of copper (general corrosion) increased with decreasing pH in the pH range 3-6.5. However, the pH of most drinking waters lies between pH 6.5 - 9.5.

Cohen and Lyman (125), on the other hand, documented that the pitting of copper in 65 U.S. waters was prevalent in the pH range 7.00 to 7.8. Mattsson and Fredriksson (135) reported that copper failure due to pitting in hot water systems occurred in waters of low pH (<7) and low bicarbonate alkalinity. These conflicting data suggest that the pH of the water alone may not be responsible for pitting. Other conditions such as the overall chemistry of the water, temperature, velocity, and the type and surface conditions of copper pipe have to be considered.

Dissolved Oxygen

Dissolved oxygen was found to be the second most significant factor in copper corrosion after chlorine residual. Referring to Figures 63-65, it is seen that the lowest rates of corrosion occurred in all deaerated systems containing no chlorine. The dissolved oxygen content of the aerated systems varied from 8.40-8.70 mg/l, while the concentration of

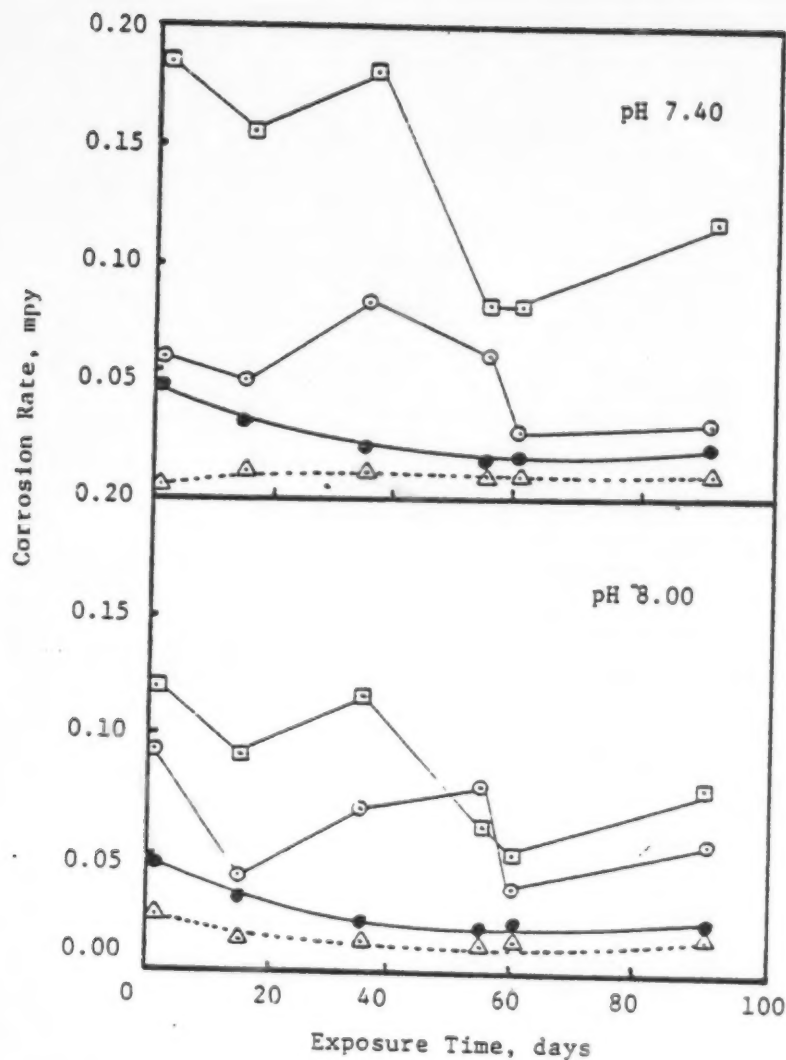


Figure 63. Rate of Corrosion of Copper Against Time. The Corrosion Rate was measured using the Corrator.

- — □ Aerated, chlorine, 1.0 mg/L
- — ○ Deaerated, chlorine, 1.0 mg/L
- — ● Aerated, no chlorine
- △ — △ Deaerated, no chlorine

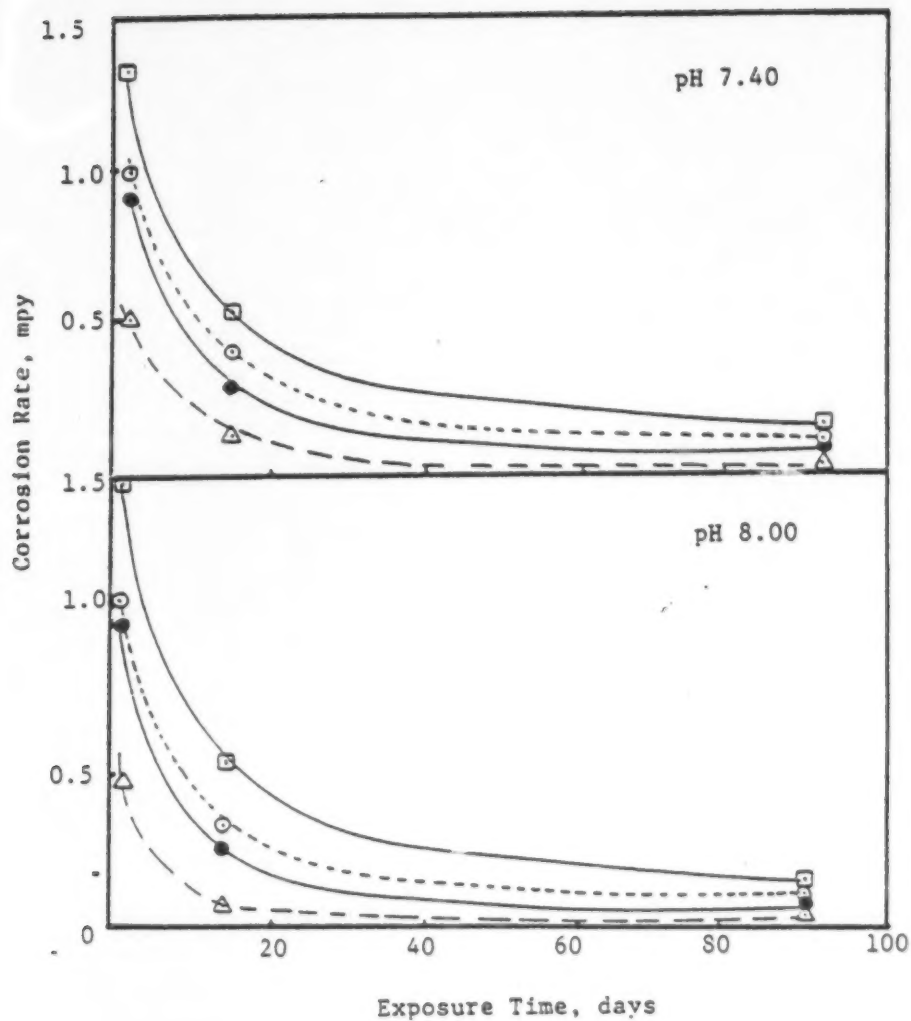


Figure 64. Corrosion Rate of Copper Against Time. The Corrosion Rate was Determined by the Weight Loss

- — □ Aerated, chlorine = 1.0 mg/L
- — ○ Deaerated, chlorine 1.0 mg/L
- — ● Aerated, no chlorine
- △ - - - △ Deaerated, no chlorine

Table 33. Average Rate of Corrosion of Copper in mpy by Corrator Method

pH	Chlorine (mg/l)	Corrosion Rate, mpy											
		1 Day		15 Day		35 Day		55 Day		60 Day		91 Day	
		A*	N	A	N	A	N	A	N	A	N	A	N
7.40	0.0	0.048	0.006	0.033	0.012	0.021	0.012	0.015	0.009	0.015	0.010	0.021	0.009
7.40	1.0	0.186	0.060	0.156	0.051	0.180	0.083	0.083	0.060	0.080	0.026	0.116	0.027
7.60	0.0	0.045	0.024	0.030	0.015	0.015	0.012	0.011	0.015	0.012	0.012	0.018	0.013
7.60	1.0	0.077	0.034	0.082	0.038	0.050	0.038	0.040	0.027	0.029	0.011	0.048	0.020
7.80	0.0	0.072	0.045	0.045	0.006	0.030	0.009	0.018	0.006	0.031	0.012	0.021	0.012
7.80	1.0	0.159	0.064	0.146	0.078	0.111	0.088	0.123	0.082	0.078	0.041	0.085	0.047
8.00	0.0	0.045	0.024	0.030	0.012	0.018	0.012	0.012	0.010	0.015	0.012	0.015	0.012
8.00	1.0	0.121	0.082	0.092	0.036	0.115	0.068	0.058	0.077	0.047	0.032	0.074	0.050

*A = Air- Saturated, N = Deaerated with N₂ gas.

Table 34. Average Rate of Corrosion of Copper,
mpy By Weight Loss Method

pH	Chlorine (mg/l)	Corrosion Rate, mpy					
		2 Days		15 Days		91 Days	
		A*	N	A	N	A	N
7.40	0.0	0.93	0.50	0.26	0.12	0.06	0.04
7.40	1.0	1.32	1.00	0.50	0.38	0.13	0.07
7.60	0.0	0.98	0.50	0.25	0.07	0.06	0.03
7.60	1.0	1.17	1.10	0.60	0.40	0.12	0.06
7.80	0.0	0.90	0.53	0.26	0.08	0.06	0.02
7.80	1.0	1.42	0.97	0.74	0.60	0.11	0.09
8.00	0.0	0.95	0.48	0.25	0.08	0.06	0.03
8.00	1.0	1.41	1.03	0.50	0.37	0.11	0.09

* A = Air-saturated, N = deaerated with N₂ gas.

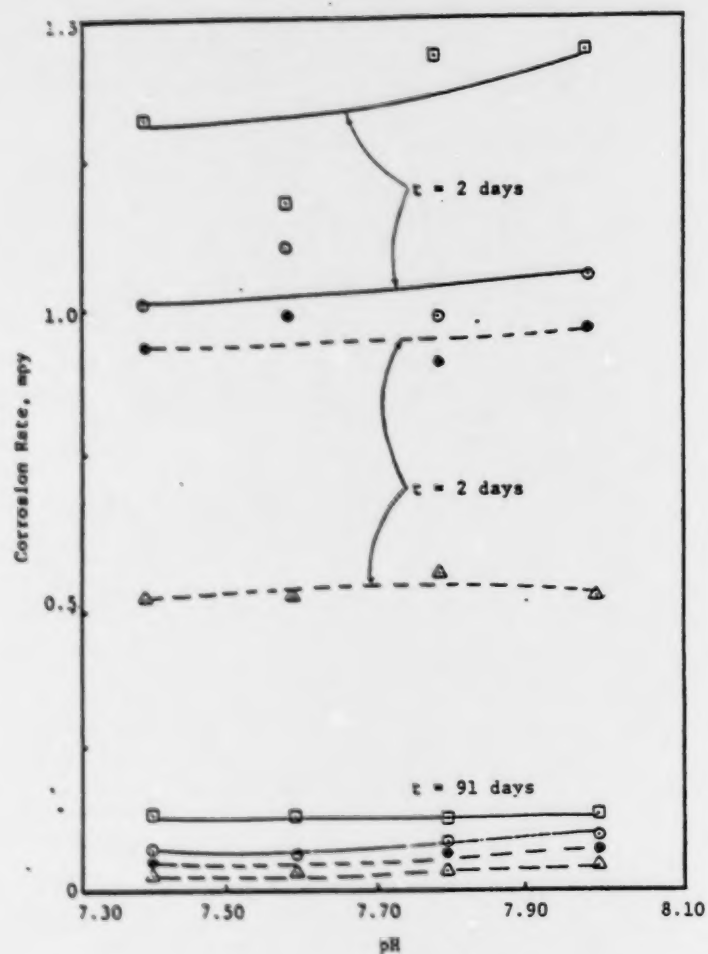


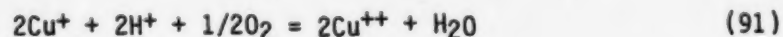
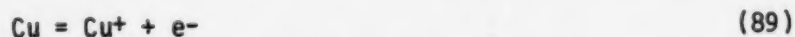
Figure 65. Corrosion Rate of Copper Against pH at Two Exposure Times. Weight Loss Method.

- — □ Aerated, chlorine = 1.0 mg/L
- — ○ Deaerated, chlorine = 1.0 mg/L
- - - - ● Aerated, no chlorine
- △ - - - △ Deaerated, no chlorine

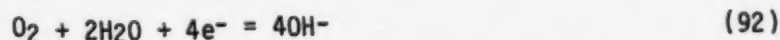
dissolved oxygen in the deaerated jars ranged from 0.1 - 0.4 mg/l. Dissolved oxygen is an oxidizing agent that is necessary for the corrosion of copper in aqueous solutions (136). The solubility of oxygen decreases with both increasing temperature and increasing mineral concentration of a solution.

Obrecht (136) showed in a series of short-term tests that oxygen was required for the corrosion of copper, implying that without the presence of dissolved oxygen, the corrosion of copper was unmeasurable. He further showed that in a closed system, the concentration of dissolved oxygen in the solution dropped as the corrosion of copper continued. When solid copper is immersed in water containing dissolved oxygen, thermodynamically, copper will corrode forming cuprous (Cu^+) and cupric (Cu^{++}) ions (127), because of the high redox potential of the solution. The anodic and cathodic reactions for copper corrosion are shown in reactions 89-92.

Anode:



Cathode:



From these reactions, it is evident that the dissolution of copper is dependent on the amount of dissolved oxygen present and the removal of dissolved copper ions either by precipitation or complexation.

Chlorine Residual

Of all the variables tested to determine their effects on the rate of corrosion of copper, chlorine residual proved to be the most important factor. Figures 63-65 indicate that the corrosion attack was severe in all chlorinated systems compared to those without chlorine. The rate of corrosion was the highest in all aerated systems containing chlorine, followed by those containing chlorine but very little dissolved oxygen (0.1 - 0.4 mg/l).

Lane and Neff (137) reported that the presence of 2 mg/L free chlorine residual was responsible for the erosion-corrosion of copper in a cold water system despite a low flow velocity.

Natural Color

The presence of natural color at 15 pcu was found to increase the rate of corrosion of copper slightly in all synthetic solutions. The effect of color on the rate of corrosion of copper in water G (Table 22) is presented in Figure 66. Similar effects were observed in the other waters.

The increase in rate of corrosion of copper in the presence of color could be attributed to the complexation of dissolved copper by color. Such an effect was not observed in the corrosion of mild steel. A possible explanation for this effect could be the slow rate of dissolution of copper, implying that as soon as the copper ions are released to solution, they are tied by color molecules. This reduces the concentration of dissolved copper in solution, thus favoring further dissolution of copper. Whereas in steel, the oxidation reaction is fast, and color is probably complexed at the initial states of exposure by ferrous ions.

Specific Ions

A series of experiments was conducted on copper specimens to evaluate the effect of chloride, sulfate and bicarbonate ions on the rate of corrosion. The chemical compounds employed in the test included NaCl, CaCl₂, and MgCl₂·6H₂O for evaluating the effect of chloride ions, while salts of Na₂SO₄, CaSO₄ and MgSO₄·7H₂O were used for preparing SO₄ solutions. In some of the tests a combination of all three compounds for each ion were used, thus the final solution contained all three cations (Na⁺, Ca⁺⁺ and Mg⁺⁺) but only one anion, either Cl⁻ or SO₄⁼. In other tests a combination of both chloride and sulfate ions were tested, both with and without alkalinity. Sodium bicarbonate was used as the source of alkalinity where applicable.

The average rates of corrosion of copper (Tables 35-36) as affected by concentrations of chloride and sulfate ions are presented in Figures 67-69. The rate of corrosion of copper after 45 days of exposure was found to be higher in chloride solutions than in sulfate solutions (Figure 67), as determined by the weight loss method. However, the Corrator data did not reveal any appreciable difference between the rates of corrosion of copper in Cl⁻ and SO₄⁼ solutions (Figure 68). The rates of corrosion, as determined by the Corrator, were significantly lower than those calculated by the weight loss method.

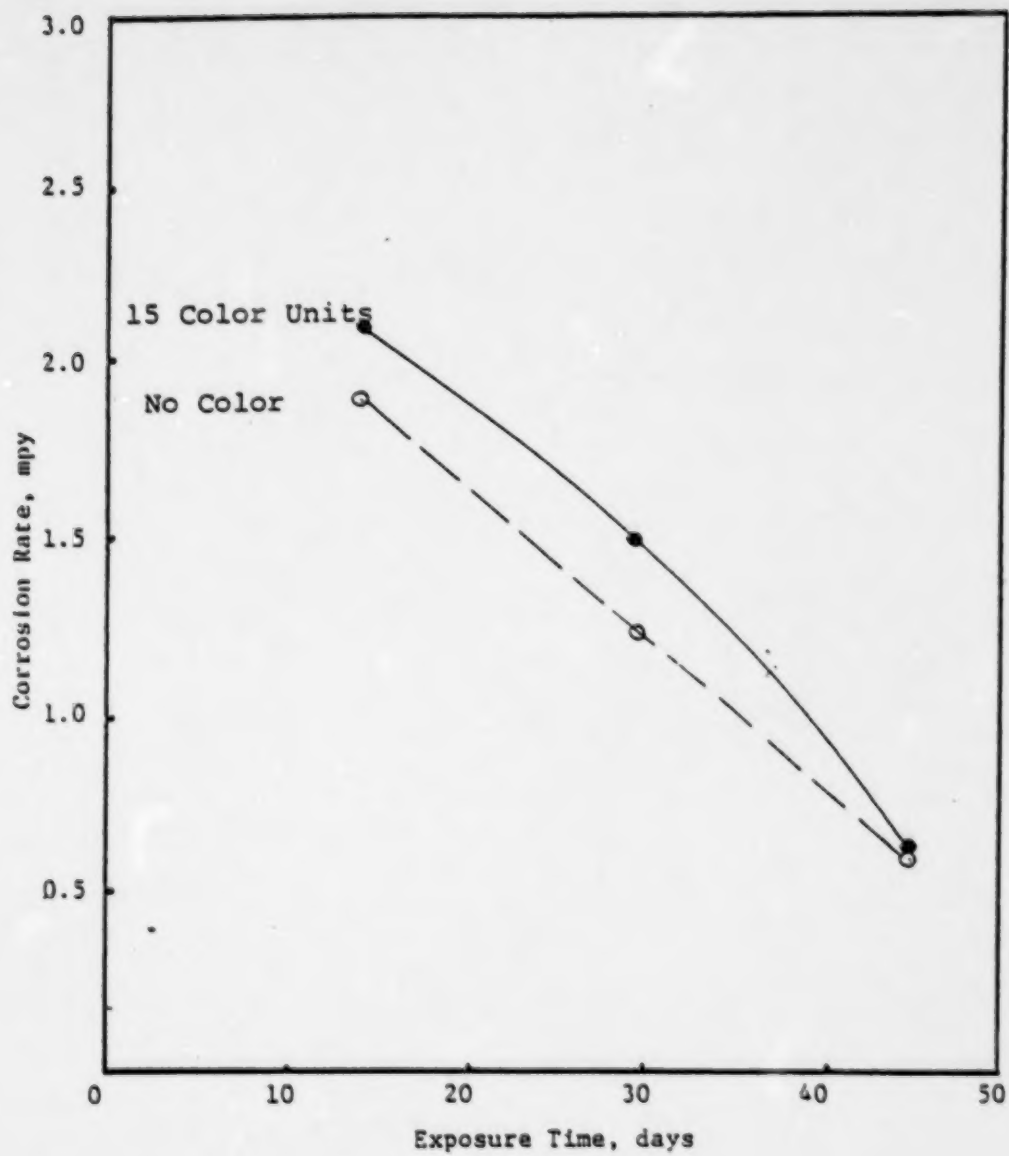


Figure 66. Effect of Natural Color on the Rate of Corrosion of Copper in Aerated Water G.

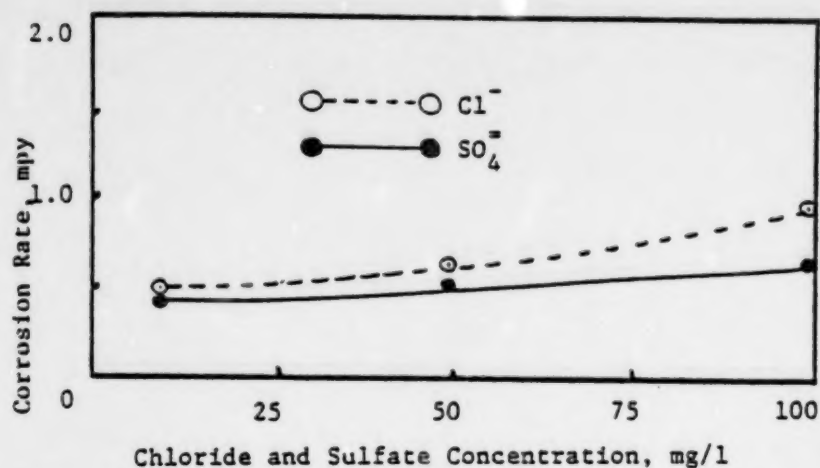


Figure 67. Effect of Chloride and Sulfate Ions on the Rate of Corrosion of Copper in Aerated Solutions, Weight Loss Method, Exposure Time 45 Days.

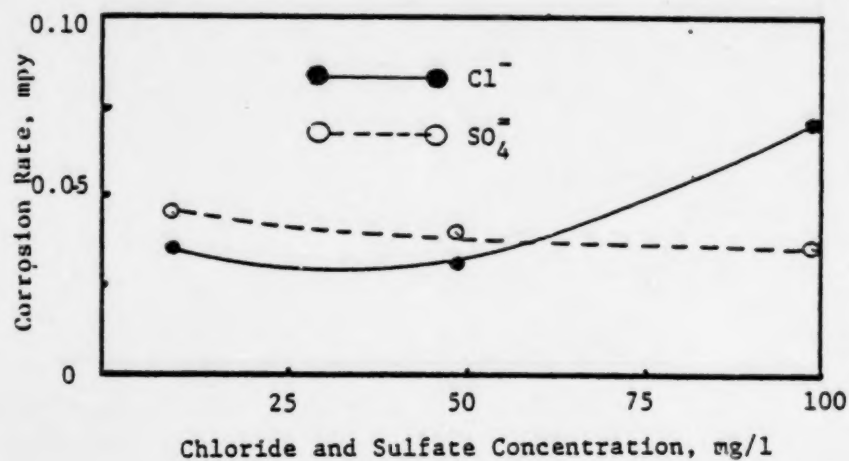


Figure 68. Effect of Chloride and Sulfate Ions on the Rate of Corrosion of Copper in Aerated Solutions. Corrotrator Method. Exposure Time 44 days.

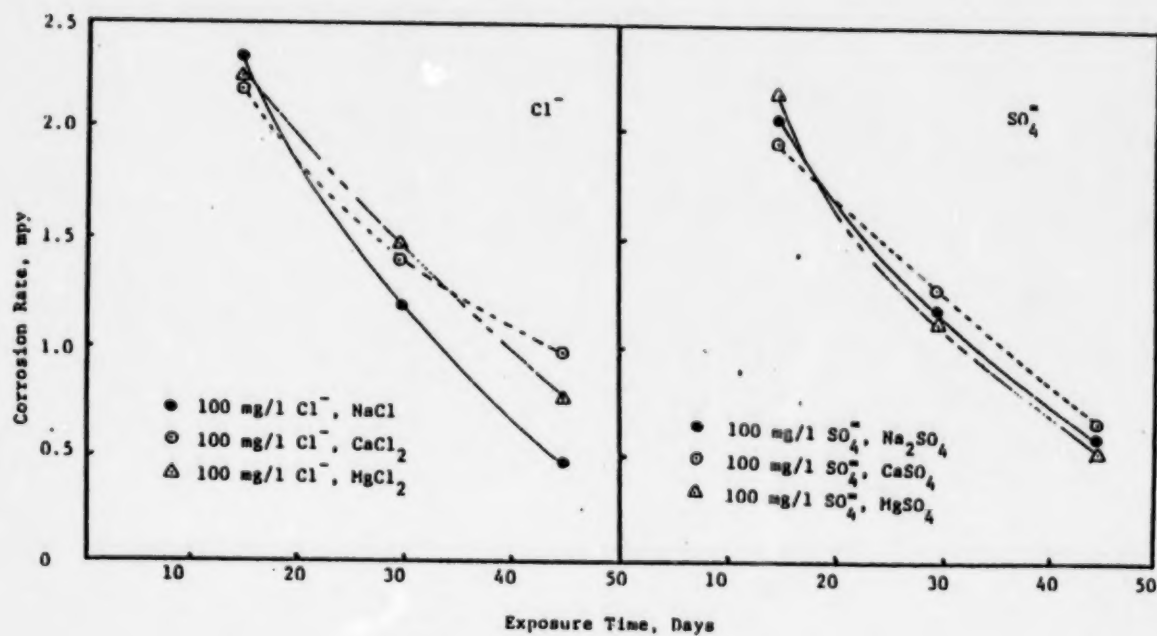


Figure 69. Effect of Chloride and Sulfate on the Rate of Corrosion of Copper in Solutions of Different Chemical Compounds.

Table 35. Average Rates of Corrosion of Copper in Chloride and Sulfate Solutions, by Weight Loss Method.

Test No.	Cl ⁻ or SO ₄ ⁼ (mg/l)	Chemical Compound	Corrosion Rate, mpy		
			15 days	30 days	45 days
1	10	NaCl	1.63	1.14	0.54
2	50	NaCl	2.12	1.27	0.75
3	100	NaCl	2.36	1.21	0.45
4	10	CaCl ₂	2.18	1.24	0.53
5	50	CaCl ₂	2.05	1.03	0.61
6	100	CaCl ₂	2.21	1.42	0.99
7	10	MgCl ₂	2.25	1.29	0.58
8	50	MgCl ₂	1.97	1.16	0.63
9	100	MgCl ₂	2.26	1.46	0.77
10	10	Na ₂ SO ₄	2.13	0.98	0.79
11	50	Na ₂ SO ₄	1.87	1.15	0.70
12	100	Na ₂ SO ₄	2.06	1.16	0.55
13	10	CaSO ₄	2.14	1.36	0.50
14	50	CaSO ₄	2.08	0.93	0.56
15	100	CaSO ₄	1.95	1.27	0.64
16	10	MgSO ₄	1.81	1.10	0.69
17	50	MgSO ₄	2.02	1.31	0.61
18	100	MgSO ₄	1.16	1.15	0.54

Table 36. Average Rates of Corrosion of Copper in Chloride and Sulfate Solutions, Measured by Corrator Probes

Test No.	Cl ⁻ or SO ₄ ⁼ (mg/l)	Chemical Compound	Corrosion Rate, mpy			
			4 days	15 days	30 days	44 days
1	10	CaCl ₂	0.09	0.08	0.07	0.07
2	50	CaCl ₂	0.24	0.14	0.09	0.06
3	100	CaCl ₂	0.81	0.66	0.54	0.14
4	10	CaSO ₄	0.23	0.21	0.20	0.09.
5	50	CaSO ₄	0.14	0.09	0.12	0.08
6	100	CaSO ₄	0.20	0.19	0.10	0.07

The effects of alkalinity on the rate of corrosion of copper (Table 37) in solutions containing both Cl^- and SO_4^{2-} ions are presented in Figure 70. Increasing alkalinity tended to decrease the rate of attack of copper, though the difference as indicated in Figure 70 was minimal.

The rate of corrosion of copper as affected by the ratio of

$$\frac{\text{Cl}^- + \text{SO}_4^{2-}}{\text{Alkalinity}}$$

where each parameter is expressed in millequivalents/L, is presented in Figure 71. Obrecht (136) showed that the corrosion of copper was not influenced by the presence of sodium carbonate (<40 ppm) and sodium bicarbonate (400 ppm), while both Cl^- and SO_4^{2-} ions were shown to increase the rate of corrosion of copper even at low concentrations. Stumm and Champlin (126), on the other hand reported that an increase in C_t , the concentration of total carbonic species, decreased the rate of corrosion of copper at a given pH value. The C_t values used (10^{-1} - 10^{-2} M) however, were far greater than those normally encountered in potable waters (10,000-1,000 mg/L as CaCO_3). Cohen and Lyman (125) in an analysis of pitting corrosion of copper reported that in 54 waters that pitted copper pipes, the concentrations of chloride were less than 75 ppm in more than 80% of the waters. However, most of these waters were high in sulfate content, approximately 3 to 4 times that of the chloride concentrations.

Redox Potential

Since corrosion of metals is an electrochemical process, and is affected by the oxidation-reduction capacity of the water, attempts were made to monitor the redox potential in selected jars. The results of redox potential measurements in the Pinellas County tap water are presented in Figure 72.

Electrode potential data in synthetic waters G and H (Table 38) are shown in Figure 73. From the data presented in Figure 72, it is evident that redox potential values in the chlorine containing systems were in direct agreement with the measured rates of corrosion in those systems. In other words, the higher the redox potential of a solution, the greater the rate of corrosion in that particular system.

Table 37. Average Rates of Corrosion of Copper as Affected by Alkalinity of Water in Aerated Solutions.

Test No.	Concentration, mg/L			Corrosion Rate, mpy		
	Cl ⁻	SO ₄	Alkalinity*	15 days	30 days	45 days
1	5	5	0	2.13	1.10	0.66
2	25	25	0	2.37	1.15	0.79
3	50	50	0	1.99	1.25	0.85
4	5	5	25	1.92	1.11	0.62
5	25	25	25	2.30	1.26	0.49
6	50	50	25	2.23	1.36	0.62
7	5	5	100	2.41	1.10	0.53
8	25	25	100	2.59	1.19	0.62
9	50	50	100	2.08	1.17	0.72
10	5	5	200	2.05	1.03	0.50
11	25	25	200	2.15	1.06	0.75
12	50	50	200	1.90	1.13	1.03

* Alkalinity is expressed in mg/l as CaCO₃. Corrosion rates determined by the Weight Loss Method.

Table 38. Redox Potential (E_H ,mv) of Copper in Aerated Waters G and H.

Water	Days							
	0	3	6	9	12	15	18	20
G	483	492	500	504	501	514	511	514
H	501	494	489	490	492	492	495	497

The measured E_H values in water H were plotted on the copper E_H - pH diagram shown in Figure 74. This Pourbaix diagram was constructed for a system containing 1.6×10^{-5} moles/L or 1.0 mg/L of dissolved copper and a total alkalinity of 100 mg/L as CaCO_3 . From pH 5.8 to about 8.2, cupric hydroxyl carbonate is the stable copper compound. Beyond pH 8.2, cupric oxide (CuO) and the species $\text{Cu}(\text{CO}_3)_2^{2-}$ begin to predominate. At this basic pH region, dissociation of bicarbonate into carbonate is more favored. Consequently, there is a higher tendency for complex-ion formation between carbonate ions and free cupric ions. In the more alkaline pH region, ($>\text{pH}10.5$), hydroxide concentration is considerably high such that hydroxylation of cupric ions is energetically favored, thus leading to the precipitation of cupric hydroxide, $\text{Cu}(\text{OH})_2$. Deposition of this salt on the copper metal surface could provide protection against corrosion. In the distribution system, however, where pH values generally range from 6.5 to 9.0, cupric hydroxyl carbonate and cupric oxide are more likely to be found in the corrosion products. All measured redox potential values coincided with the region of stability of $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$, implying that corrosion of copper will be stifled due to the passive films as long as the film is not damaged or removed from the copper surface.

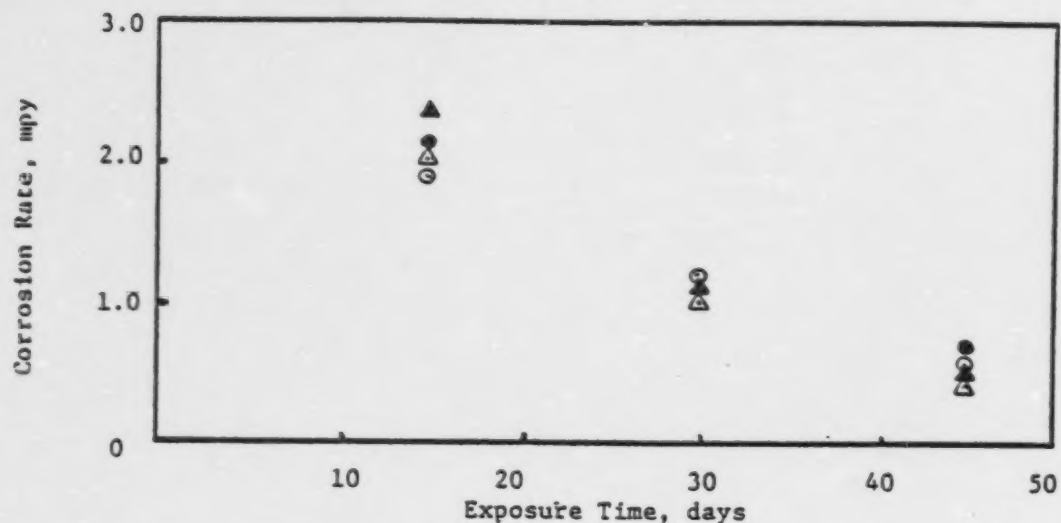


Figure 70. Effect of Bicarbonate Alkalinity on the Rate of Corrosion of Copper in Aerated Solutions Containing 5 mg/L of Chloride and Sulfate Ions.

- No Alkalinity
- 25 mg/L Alkalinity as CaCO_3
- ▲ 100 mg/L Alkalinity as CaCO_3
- △ 200 mg/L Alkalinity as CaCO_3

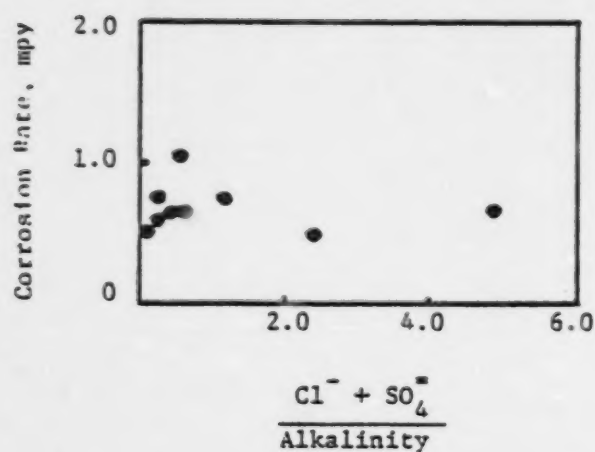


Figure 71. Effect of $\frac{\text{Cl}^- + \text{SO}_4^{2-}}{\text{Alkalinity}}$ on the Rate of Corrosion of Copper in Aerated Solutions.

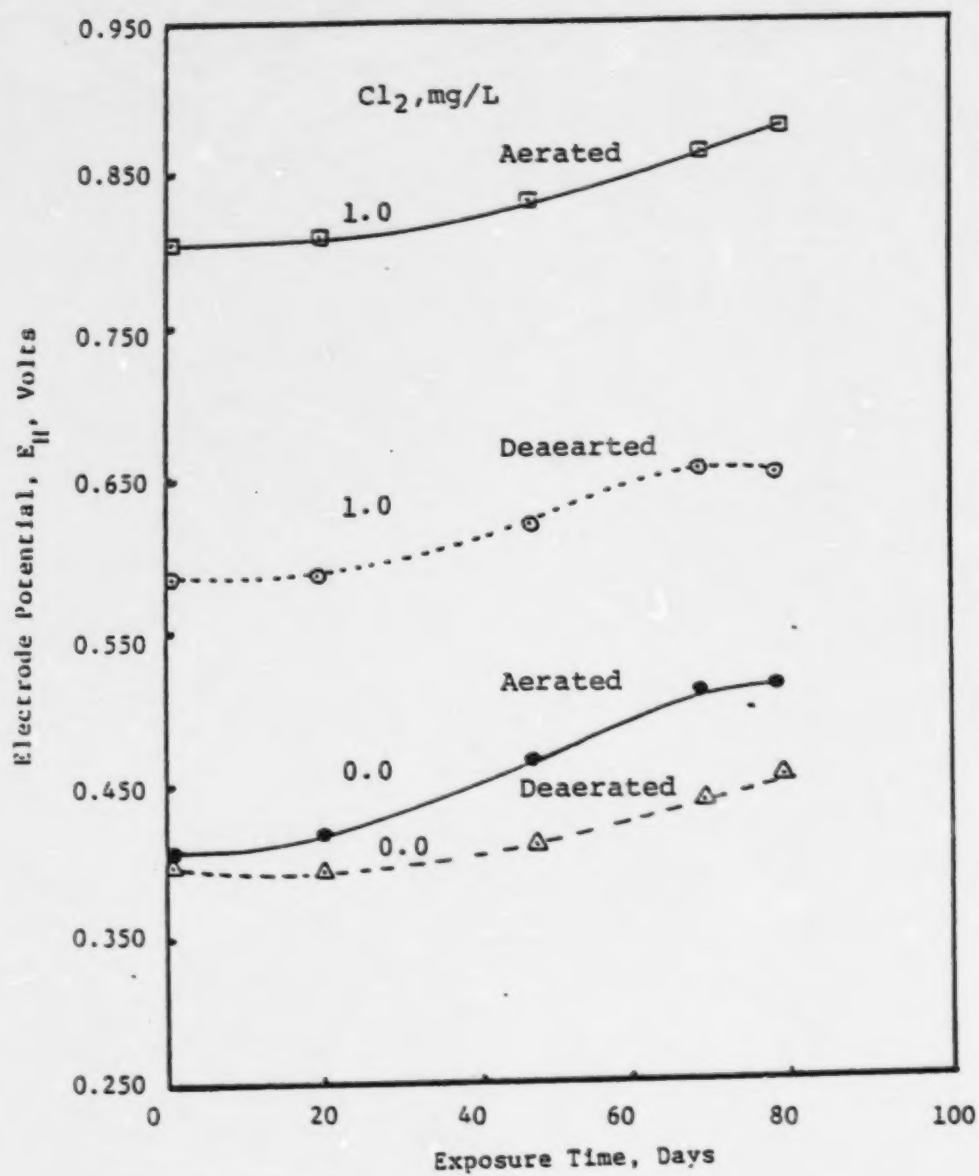


Figure 72. Redox Potential of Copper Corrosion Solutions Against Time at pH 7.40

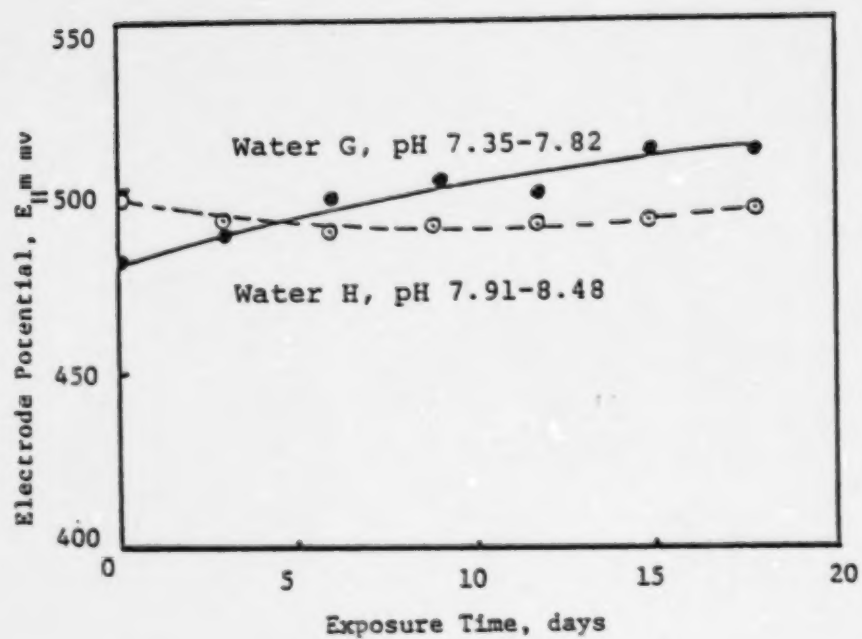


Figure 73. Variation in Redox Potential of Copper in Aerated Waters G and H.

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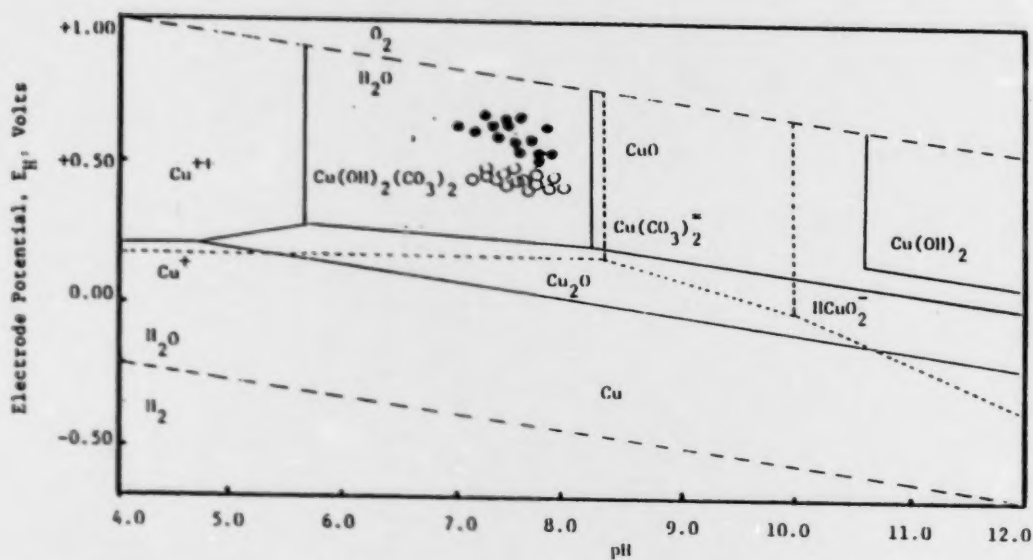


Figure 74. Pourbaix Diagram for 1.6×10^{-5} , Cu in the Presence of 100 mg/l Alkalinity as CaCO_3 , with Measured E_H Values. ● Aerated ○ Deaerated

Variation in Water Quality

In addition to analyzing the water for leaching of copper from the coupons, other water quality parameters were also monitored periodically. Dissolved oxygen, chloride, sulfate and magnesium did not vary appreciably during the tests, while both calcium and alkalinity decreased with increasing exposure time. Sodium ion increased in those jars to which NaOH was added for pH adjustment. The addition of NaOCl for maintaining chlorine residual in solutions also increased sodium in all chlorinated jars. The leaching of copper into solution is presented in Figure 75. The dissolution of copper appears to be greater in the initial stages of exposure and decreases with increasing time, possibly due to buildup of passive films on the copper surfaces.

The Nature of Corrosion

Copper pipes in domestic waters normally corrode by pitting, erosion corrosion or impingement attack (125,138,139). Pitting of copper is a common form of corrosion in potable waters. Cruse and Pomeroy (140) reported that certain Southern California waters pitted copper pipes so badly that failure occurred in less than one year after being in operation. The pH of the waters that support pitting was in the range 6.6-7.5, with medium to high mineral content. In other waters copper pipes were more resistant to pitting attack, lasting more than forty years. Several factors were described as the cause of this rapid pitting. Some of the factors are related to the chemistry of the water, such as pH, redox potential and the type and amount of minerals. Others are related to the metal itself, such as its surface condition and the homogeneity of the oxide film. Many other factors depend on the operation and design of the system, including velocity of flow, temperature and the quality of workmanship (125).

Impingement attack is usually characterized by roughening of the inside surface of the copper tube, due to high flow velocity and entrained solids or gases (125). The mechanism and theory of pitting of copper in drinking waters has been investigated by Lucey (141), Mattsson (142,143) and Mattsson and Fredriksson (135). Lucey (141) postulated the "membrane cell theory" (141) which states, "pitting arises when a pocket of cuprous chloride forms beneath a porous of electrically conducting membrane (usually cuprous oxide). The anodic and cathodic processes occur on the inner and outer surfaces of the membrane. Dissolution of copper occurs by reaction of hardness salts in the water with the cathodic product above the membrane" (141,144). The proposed model of pitting of copper, as described by Lucey is shown in Figure 76.

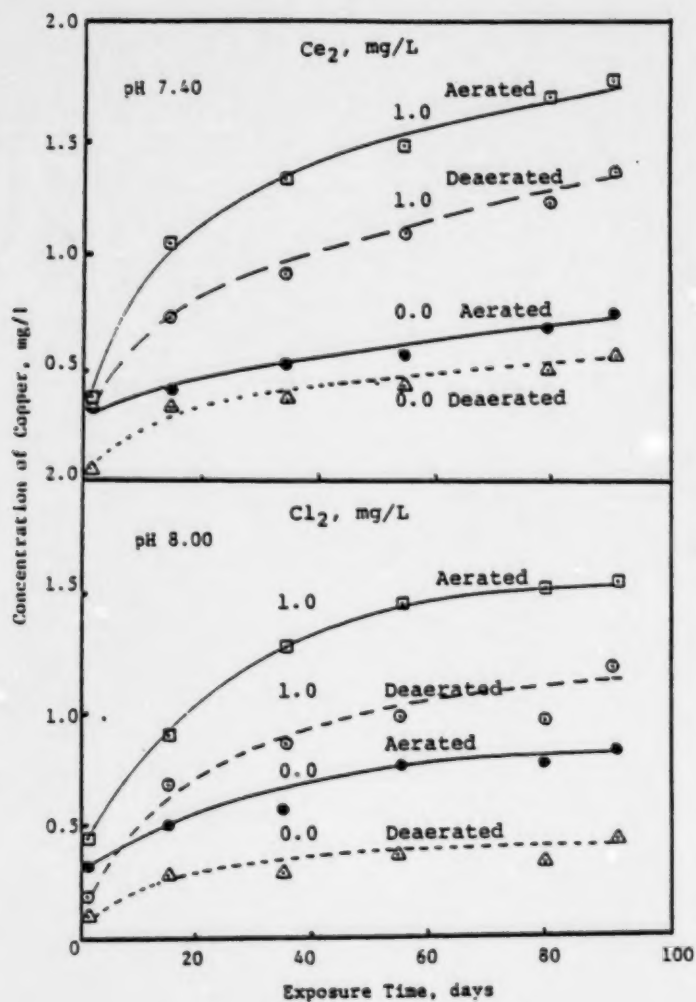


Figure 75. Increase in Concentration of Soluble Copper in Test Waters Due to Corrosion.

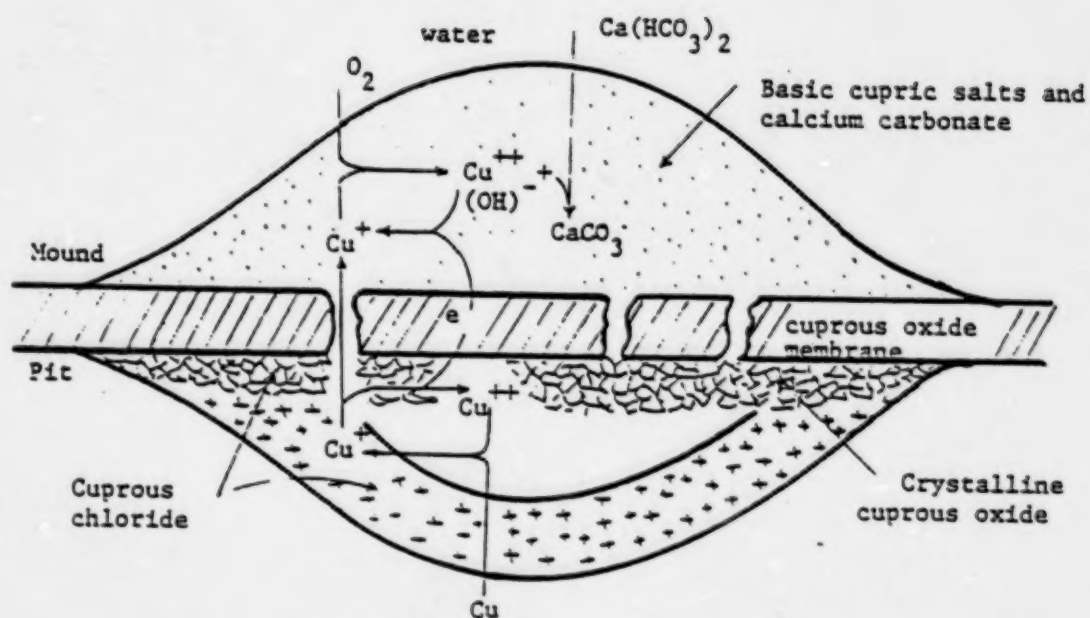
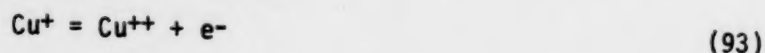
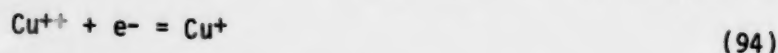


Figure 76. Pitting Corrosion of Copper (141).

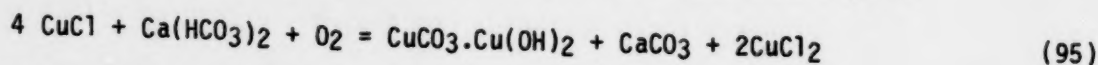
Figure 76 shows the structure of the pit, comprised of a mound, a cuprous oxide membrane and a cuprous chloride pocket. The anodic and cathodic reactions that occur on the inner and outer surfaces of the pit are shown in Eq. 93-95. The anodic reaction that takes place on the inner surface of the membrane (Eq. 93) is



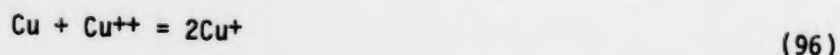
While the cathodic reaction on the outer surface of the oxide membrane (Eq. 94) is



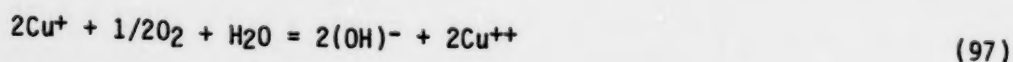
Other reactions that occur inside and outside the pit are illustrated in Eq. 95-97. The anodic reaction that takes place, within the mound above the pit, as influenced by the water quality is shown in Eq. 95.



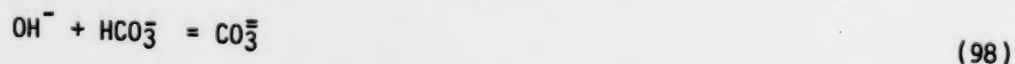
The anodic product of reaction 95 reacts with copper within the pit to generate cuprous ions (Eq. 96).



The role of both chloride and oxygen in pitting of copper are evident as shown in reaction 95-97. The effect of oxygen on the oxidation of cuprous chloride to cupric chloride (Eq. 97) and the production of cuprous chloride by cupric ions (Eq. 96) are also influenced by the alkalinity of the water (141).



The hydroxyl ions that are generated due to the reduction of oxygen, react with carbonate alkalinity (Eq. 97) to form carbonate that precipitates calcium above the pit in the crust (Eq. 98).



The hydroxyl ions also react with cupric ions and carbonate ions, resulting in the formation of basic copper carbonate.

Mattsson (142) separated the pitting of copper in fresh waters into two types, according to the temperature of the system. Type I, that occurs in cold waters, and Type II that is common in hot water installations. The main causes of pitting in Type I were described to be the presence of

either a carbonaceous film, or a deposit of solid CuCl on the surface of the copper. In addition the oxide membrane theory proposed by Lucey (141) was used to explain Type I pitting. No mechanism for Type II pitting of copper has been proposed. Type II pitting of copper has been shown to be influenced by the pH of the solution and the sulfate content of the water. The ratio of $\text{HCO}_3^-/\text{SO}_4^{2-}$ has also been shown to affect Type II pitting. The lower this ratio, the greater the pitting tendency of copper (142).

Corrosion Studies in Circulating Systems

Mild steel and black steel pipes were used in the loop system to evaluate the effects of water velocity and saturation index of the water on corrosion rates. The water quality changes during the corrosion studies were monitored.

Influence of Water Velocity on the Corrosion of Mild Steel

Mild steel pipes with different internal diameters were installed in the PVC sample holder section of the loop system. The length of each steel pipe was 2.0 inches and the internal diameters were 1.0, 0.75, and 0.50 inch. With the aid of a varistaltic pump, the rate of flow of the circulating water was regulated to give linear flow velocities of 0.38, 0.67, and 1.52 meters/minute. Water C, whose analysis is presented in Table 18, was circulated throughout the loop system with $\text{DO} = 9.0 \text{ mg/l}$ for 20 days. The corrosion rate, expressed in weight loss per square dm per day, at different exposure periods is presented in Figure 77. With increase in water velocity, the corrosion rate also increased. Consistent with the findings in the jar tests, higher corrosion rates were observed when the contact time of the mild steel with the water was shorter. Calculations showed that corrosion rate at a linear velocity of 0.38 meter/minute after the first day was about 88% higher than those with the same velocity after 5, 10, and 20 days. There was a small difference in corrosion rates among those in the 5th, 10th, and 20th day at a 0.38-meter/minute velocity. The difference, however, tended to become larger when higher flow velocities of 0.67 and 1.52 meter/minute were considered. Relative to the corrosion rate after 20 days at a flow velocity of 1.52 meter/minute, corrosion was faster by 85% after 1 day, 16% after 5 days, and 3% after 10 days. Other investigators also found higher corrosion rates when the water velocity was increased. The corrosion-time

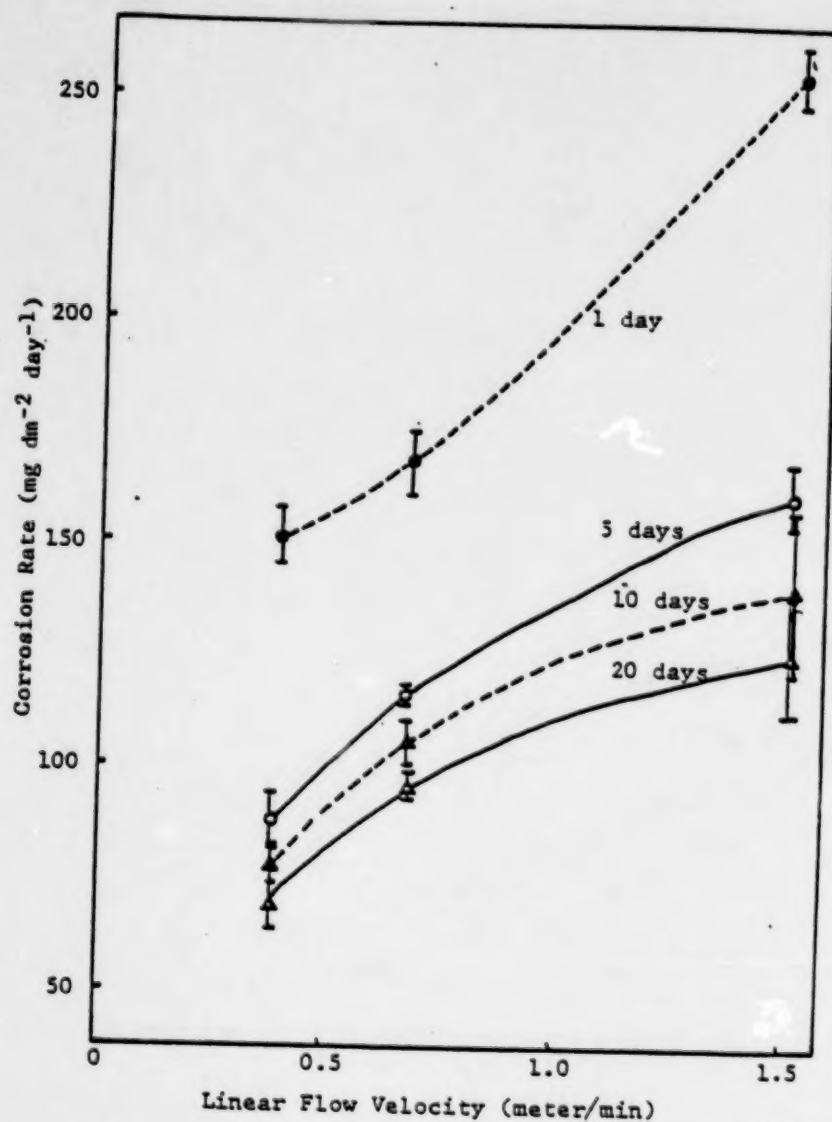


Figure 77. Variation of Corrosion Rates of Mild Steel with the Linear Flow Velocity of Water at Different Exposure Times. Water C was Used in the Loop System with 9.0 ± 0.2 mg/l Dissolved O₂. The Bar Indicates ± 1 Standard Error.

curves obtained by Butler and Stroud (145,146) for mild steel exhibited increases in corrosion rates as the water flow rate was increased from 2.4 to 4.0 feet/minute.

The increase in corrosion rate with water velocity could be attributed to the increase in turbulence and mechanical stress or erosion effect of fast moving waters. Under an increasingly turbulent condition, the deposition of corrosion products on the metal surface is inhibited. Some of these corrosion products cannot adhere to the metal, thus, making the metal more vulnerable to further corrosive attack. Even though there is a possibility that the corrosion products could lay a protective coating on the metal surface, further increase in velocity could easily remove the freshly deposited layer resulting in enhanced corrosion. When certain portions of the metal surface are bared and the rest are covered with corrosion products, further corrosive attacks could be initiated. Since the metal surface is not uniform, localized corrosion cells could easily be established which could lead to severe corrosion damage.

Corrosion of Black Steel Pipes in Waters with Different Saturation Indices

Four black steel pipes (1-inch diameter) were used for the entire 21-day corrosion experiment for each water circulated at a flow velocity of 0.38 meter/minute in the loop system. Each of the five synthetic waters, whose analyses are presented in Table 18, was used in each run with a dissolved oxygen content of 5.0 ± 0.2 mg/l. At appropriate time intervals, aliquots were withdrawn from the reservoir containing 54.6 liters (30 gallons) of water for analysis. Figure 78 shows the bar diagram indicating the extent of corrosion in terms of weight loss per cm^2 of metal for each water. The highest weight loss occurred in water B (SI = -0.46) followed by those for water A (SI = -0.72) and water F (SI = +0.94). Water C (SI = +0.57) and water D (SI = +0.04) have comparable corrosion rates and have the lowest weight loss among the five waters used. Again, the results showed that there is no linear relationship between corrosion rate and saturation index. Similar to the results in the jar tests, waters with increasing negative SI were not necessarily corrosive. Likewise, waters with high positive SI did not yield lower corrosion rates. Using the usual interpretation for the Langelier Index or SI, water A would have appeared as the most corrosive, yet its corrosivity was comparable with water F with a positive SI. Water F would have been expected to be the least corrosive; nevertheless, it was more corrosive than waters D and E with lower positive SI values. Aside from the saturation index, other important water quality factors would have to be considered in accounting for the aggressive properties of waters towards metals.

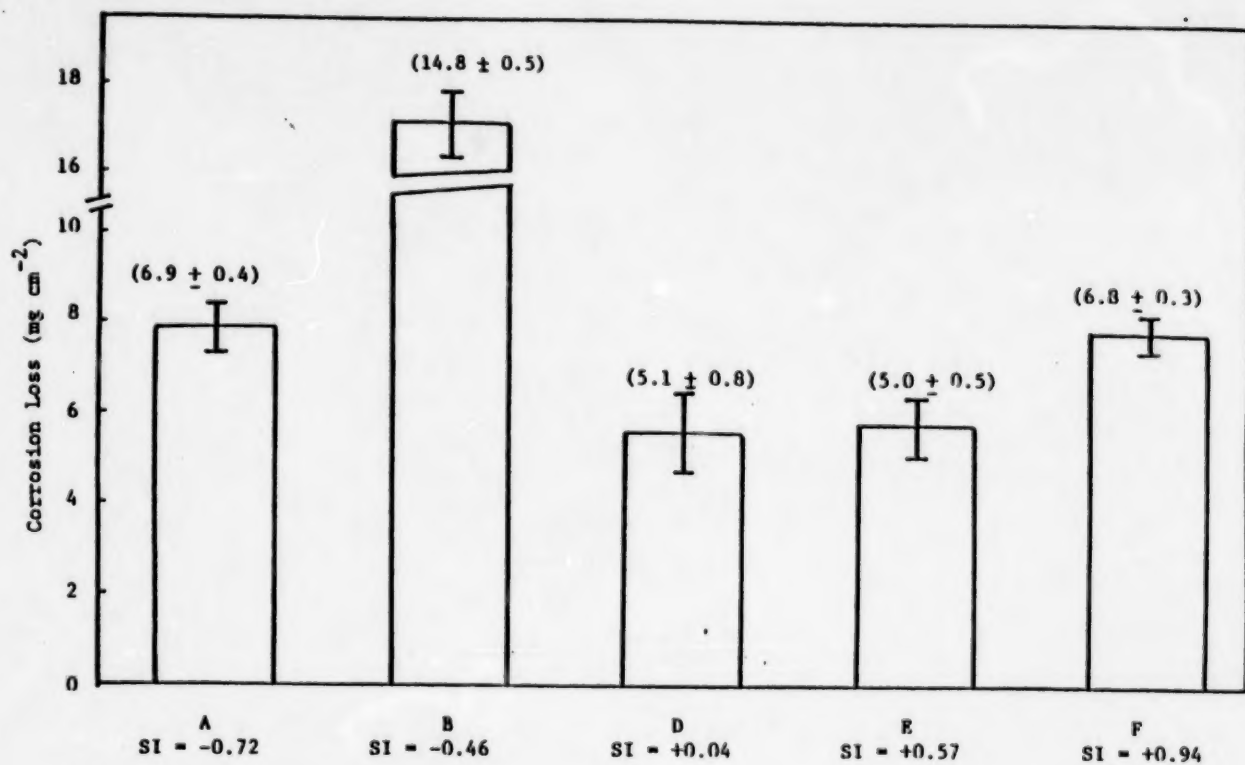


Figure 78. Bar Graph Showing the Corrosion Loss from Black Steel Pipes After 21 days in the loop System Using Five Waters of Different Saturation Indices. Indicates $\pm$ One Standard Error. Number Inside the Parenthesis Above Each Bar Refers to Corrosion Rate in Mils Per Year (mpy).

Changes in Water Quality During Corrosion of Steel Pipes

While the dissolved chemical constituents of a water are important in determining to a certain extent its corrosivity to the metal, it is essential to know how the water quality changes due to corrosion. The results of the water quality monitoring for the first loop studies using water C at different flow velocities are shown in Figures 79 and 80. No significant changes were found in the concentrations of magnesium, sodium, chloride, and sulfate ions. Only Ca^{+2} and dissolved iron exhibited significant concentration variation with time. Ca concentrations did not change for the first day but showed a decrease after 5 days and then a minimal decrease on the 10th and 20th day. The decrease in Ca^{+2} was probably due to the precipitation of CaCO_3 although adsorption of Ca^{+2} by hydrous oxides of iron is possible (147) and might account for its small decrease. The saturation index of water C was -0.35 which would mean a reduced tendency for calcite formation, but localized pH increase in the cathodic regions of the corroding metal surface could promote CaCO_3 deposition. Dissolved iron, which was not initially present, started to increase after the first day and then continued to increase up to the 10th day and then began to fall off on the 20th day. The increase of iron concentration was indicative of faster leaching of ferrous ions due to the rapid corrosion rate. Iron concentration decreased later because the corrosion rate was slowing down and some of the ferrous ions were being oxidized and precipitated out of the solution to combine with the corrosion products. Although magnesium remained almost constant, the total hardness of the solution continuously went down as shown in Figure 80. The decrease in total hardness was, of course, a reflection of the decrease of Ca, a major hardness cation. Both pH and alkalinity dropped which indicated that a certain portion of the alkalinity had been consumed during the formation and condensation of corrosion products. When CO_3^{-2} reacts with Ca^{+2} and Fe^{+2} to form carbonate salts, the HCO_3^- equilibrium is shifted to the production of more CO_3^{-2} with the release of hydrogen ions that accounts for the lowering of pH. Continuous pH decrease was also observed in kinetic studies of CaCO_3 precipitation in aqueous systems (148,149). The buffer capacity, on the other hand, went down initially but started to increase slightly after 10 days. The initial decrease was due to the predominant effect of the lowering of alkalinity. However, later the pH effect became overwhelming so that when the pH became lower and the change in alkalinity was minimal, the buffer capacity increased.

The results of water quality monitoring during corrosion of black steel pipes in the loop system are presented in Table 39. The analytical parameters which did not exhibit significant changes were not listed. These parameters are magnesium, sodium, chloride, and sulfate. Generally, there was a consistent decrease in calcium, alkalinity, and hardness

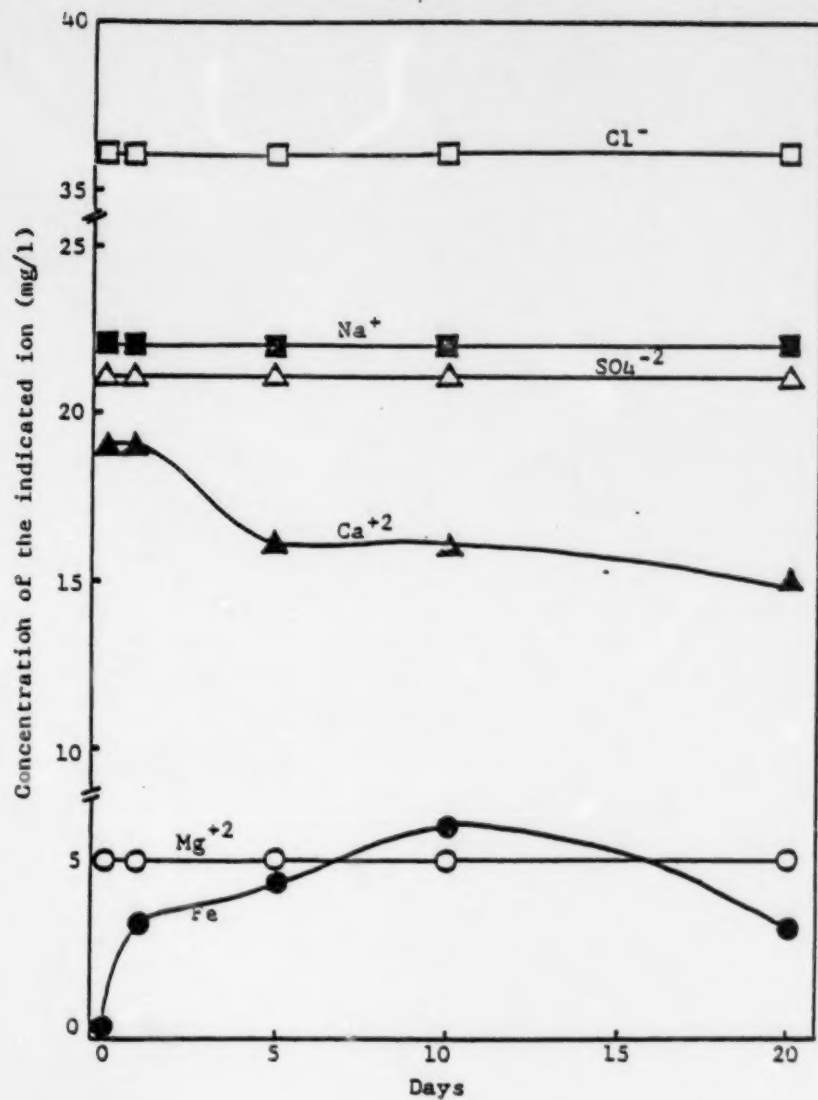


Figure 79. Changes in Concentration with Time of the Major Cations and Anions of Water C and the Dissolved Iron Leached from the Corroding Mild Steel Pipes.

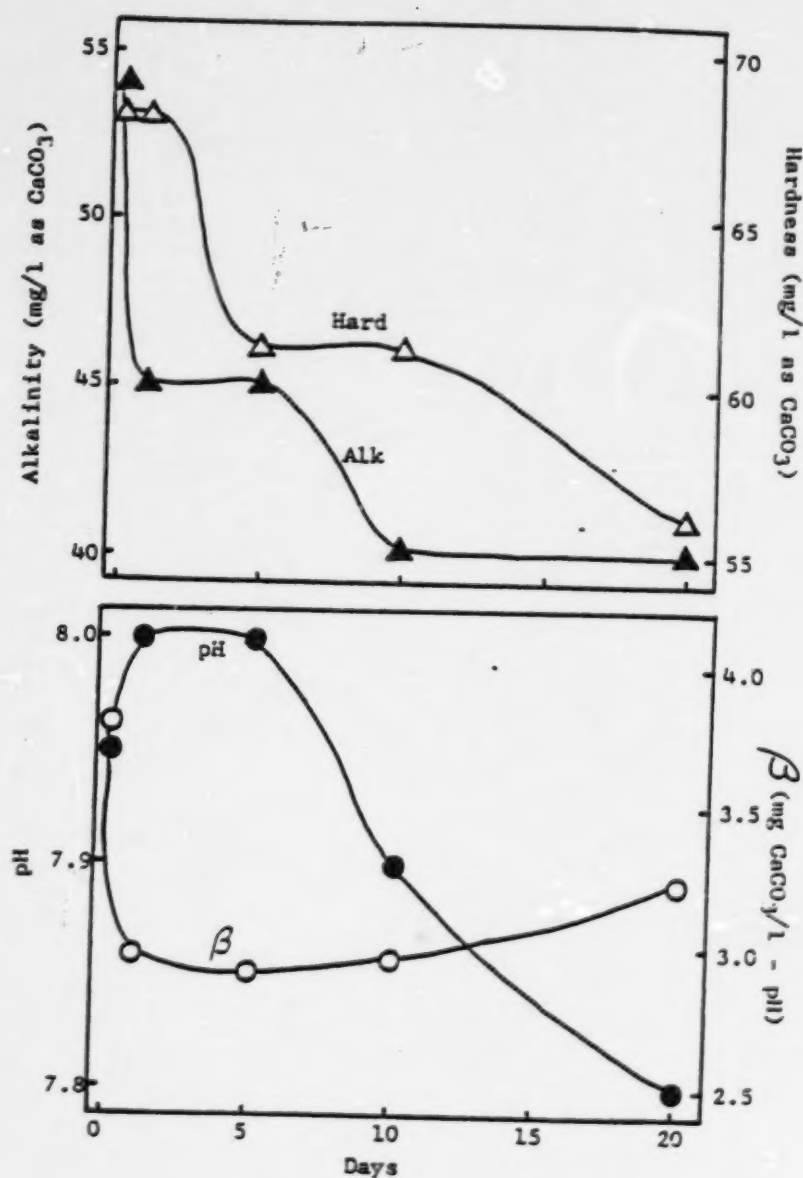


Figure 80. Changes with Time of Alkalinity, Hardness, pH, and Buffer Capacity (β) of Water C Used in the Loop System with Mild Steel Pipes.

Table 39. Water Quality Changes During a Twenty-One-Day Experimental Run for Each Water in the Loop System Using Black Steel Pipes

	Days	Ca*	Alk†	Hard†	pH	pHs	SI	β^{**}	Cond††	Fe***
Water A	0	26	60	81	7.50	8.22	-0.72	10	261	0
	3	20	56	66	7.40	8.37	-0.97	11	280	24
	10	18	54	61	7.20	8.43	-1.23	16	277	96
	21	18	49	61	7.20	8.47	-1.27	15	271	112
Water B	0	40	148	170	7.25	7.71	-0.46	40	660	0
	3	36	133	152	6.75	7.80	-1.05	89	770	26
	10	34	129	147	7.40	7.84	-0.44	25	590	40
	21	33	128	144	7.40	7.85	-0.45	25	639	162
Water D	0	15	94	99	8.35	8.31	+0.04	4	405	0
	3	14	93	97	8.20	8.34	-0.14	5	410	32
	10	12	92	92	8.05	8.41	-0.36	6	415	42
	21	12	90	92	8.05	8.42	-0.37	6	400	112
Water E	0	120	91	353	8.00	7.43	+0.57	6	870	0
	3	95	79	291	7.45	7.63	-0.18	14	880	16
	10	89	74	268	7.45	7.69	-0.24	16	910	38
	21	84	71	255	7.50	7.73	-0.23	15	895	104
Water F	0	78	159	319	8.35	7.41	+0.94	8	950	0
	3	59	142	271	7.85	7.59	+0.26	12	960	30
	10	58	139	260	7.75	7.60	+0.15	14	870	41
	21	52	135	245	7.60	7.66	-0.06	18	875	102

* Ca in mg/l.

† Alkalinity (Alk) and Hardness (Hard) in mg/l as CaCO_3 .

** Buffer capacity (β) in mg CaCO_3 /l-pH.

†† Conductivity (Cond) in $\mu\text{mho/cm}$.

*** Dissolved iron in $\mu\text{g/l}$.

reflecting CaCO_3 precipitation. Part of the decrease in alkalinity could be attributed to the reaction of CO_3^{2-} ions with Fe^{2+} , especially in the waters with sufficiently high alkalinity. Except for water B, there was a continuous decline in pH for all the waters tested. The pH of water B decreased after 3 days but increased after 5 and 10 days. Although this may be unexpected, there is a possibility that some precipitated carbonate salts of calcium and iron might have dissolved and thus contributed to a pH rise. The buffer capacity and conductivity showed a comparable pattern of change, that is, they increased initially and then decreased later. The amount of dissolved iron continuously increased. With the change of calcium, alkalinity, and pH, the CaCO_3 saturation state of the water similarly changed. The signs and magnitudes of all the stabilities of the waters were different from the initial values. The SI values of waters A and B became increasingly negative, while those of waters D, E, and F changed from positive to more negative SI. The results indicate that like pH, Alk, and pHS, SI is also time dependent which has important implications that the CaCO_3 -precipitating or dissolving tendency could change whenever corrosion commences. As localized corrosion cells are created on the metal surface and differences in chemical properties between the bulk solution and catholyte or anolyte becomes significant, there could be both spatial and temporal variation of SI in the system. Hence, basing the corrosivity of a water solely on saturation index would be inadequate and would appear confusing. The sign and magnitude of SI for a water leaving a treatment plant could be very different once it comes in contact with a corroding unprotected metal surface inside the distribution system especially if the contact time is long enough.

Analysis of Corrosion Products from Mild and Black Steel Pipes

The corrosion products from mild steel and black steel pipes were subjected to X-Ray diffraction analysis. Figures 81, 82, 83, and 84 show the X-Ray patterns of the corrosion products of mild steel collected after 1, 5, 10, and 20 days. The major peaks correspond to two forms of iron oxides, namely magnetite (Fe_3O_4) and lepidocrocite ($\gamma\text{-FeOOH}$), and two forms of calcium carbonate, calcite [$\text{CaCO}_3(\text{c})$] and aragonite [$\text{CaCO}_3(\text{a})$]. Aragonite was absent in the corrosion products after the first day, but appeared later after 5, 10, and 20 days. The precipitation of CaCO_3 was quite surprising since the saturation index of the water C was -0.35. However, consideration of the microscale effect of the relatively high pH in the cathodic zones would explain the presence of CaCO_3 in the corrosion products and the decrease of calcium concentration and alkalinity of the solution. Due to the production of OH^- ions from the cathodic reduction of dissolved oxygen, HCO_3^- could be neutralized by OH^- to form

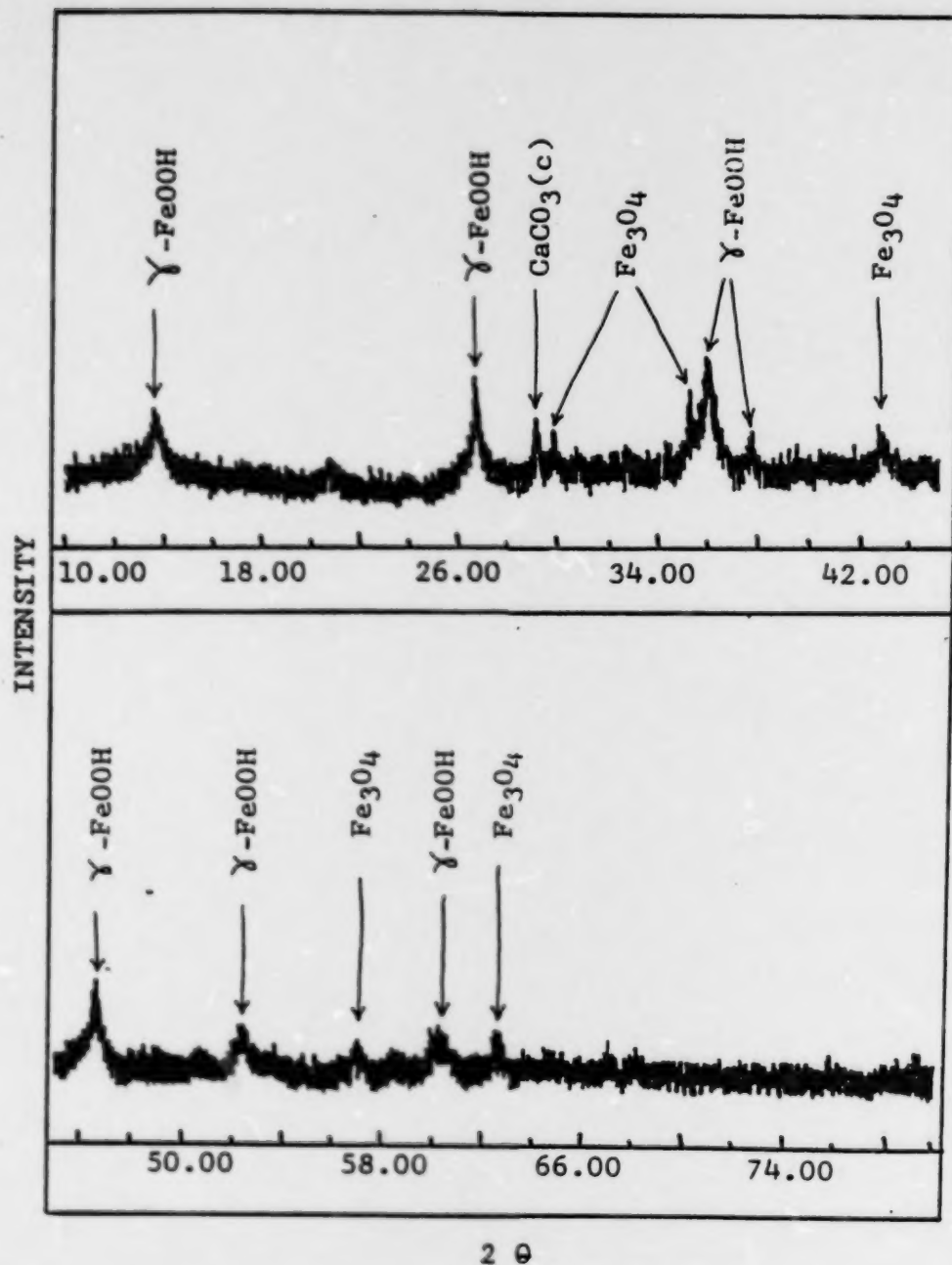


Figure 81. X-Ray Diffractogram of the Corrosion Products of Mild Steel Pipes After 1 Day.

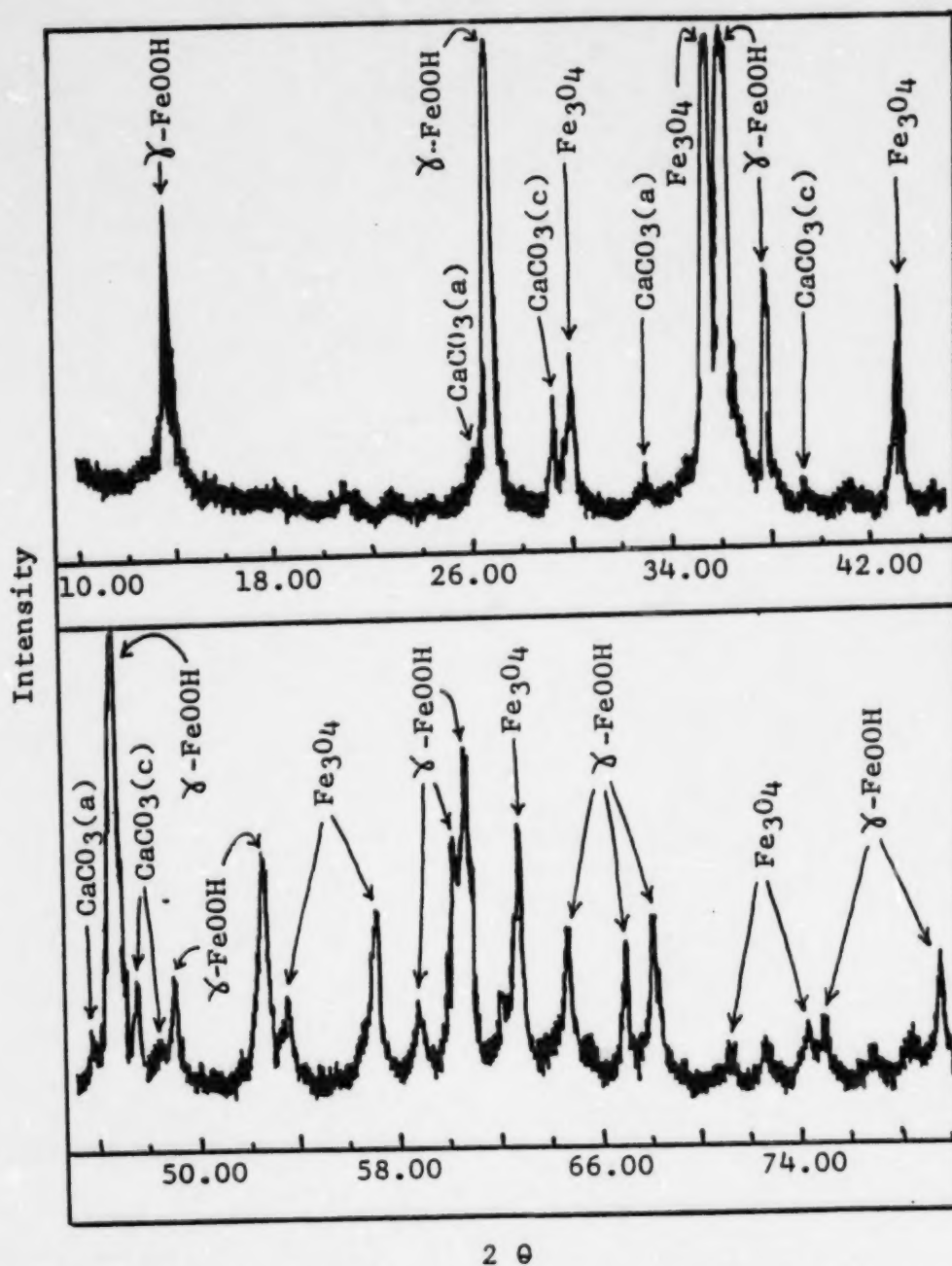


Figure 82. X-Ray Diffractogram of the Corrosion Products of Mild Steel Pipes After 5 Days.

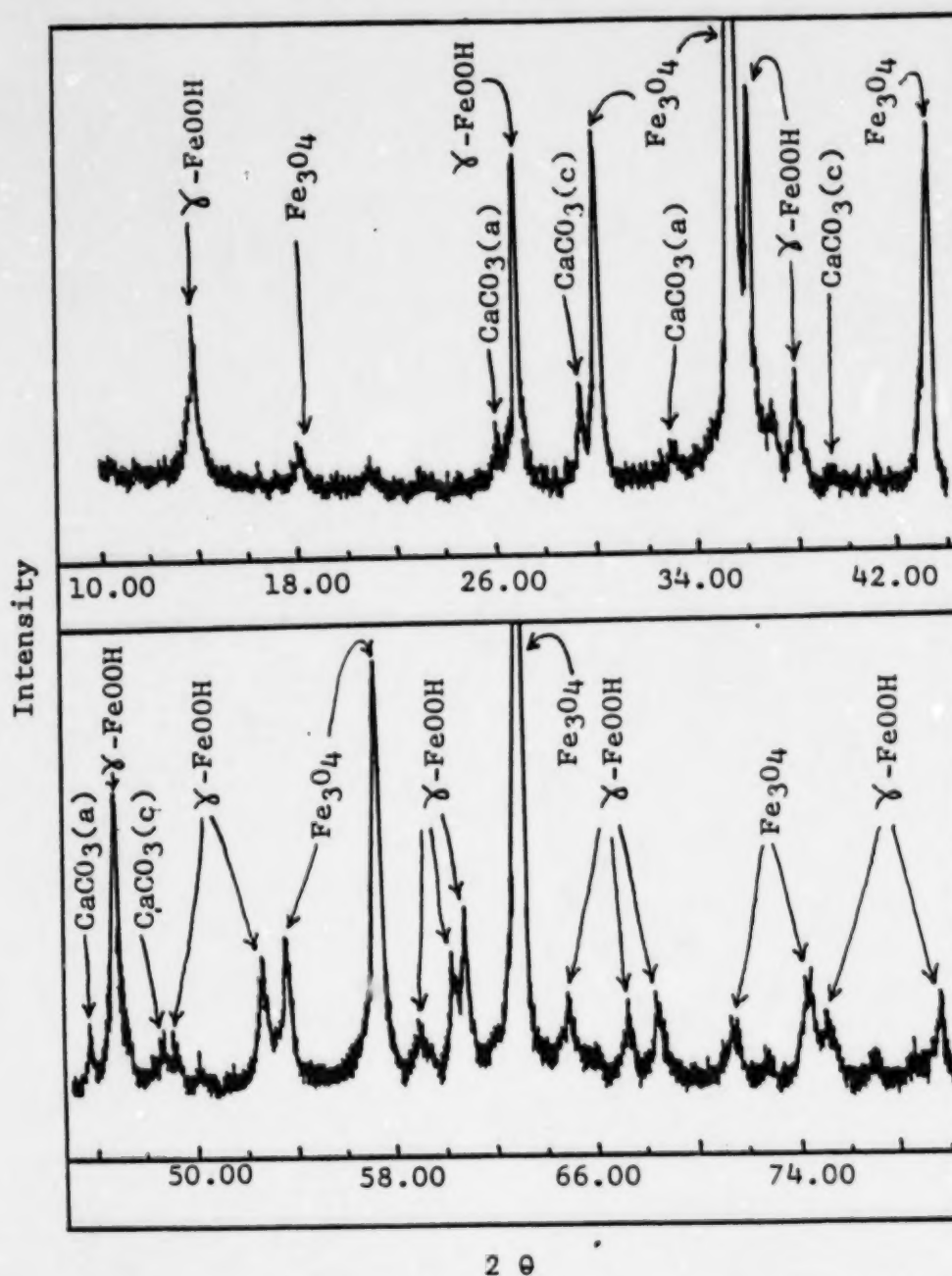
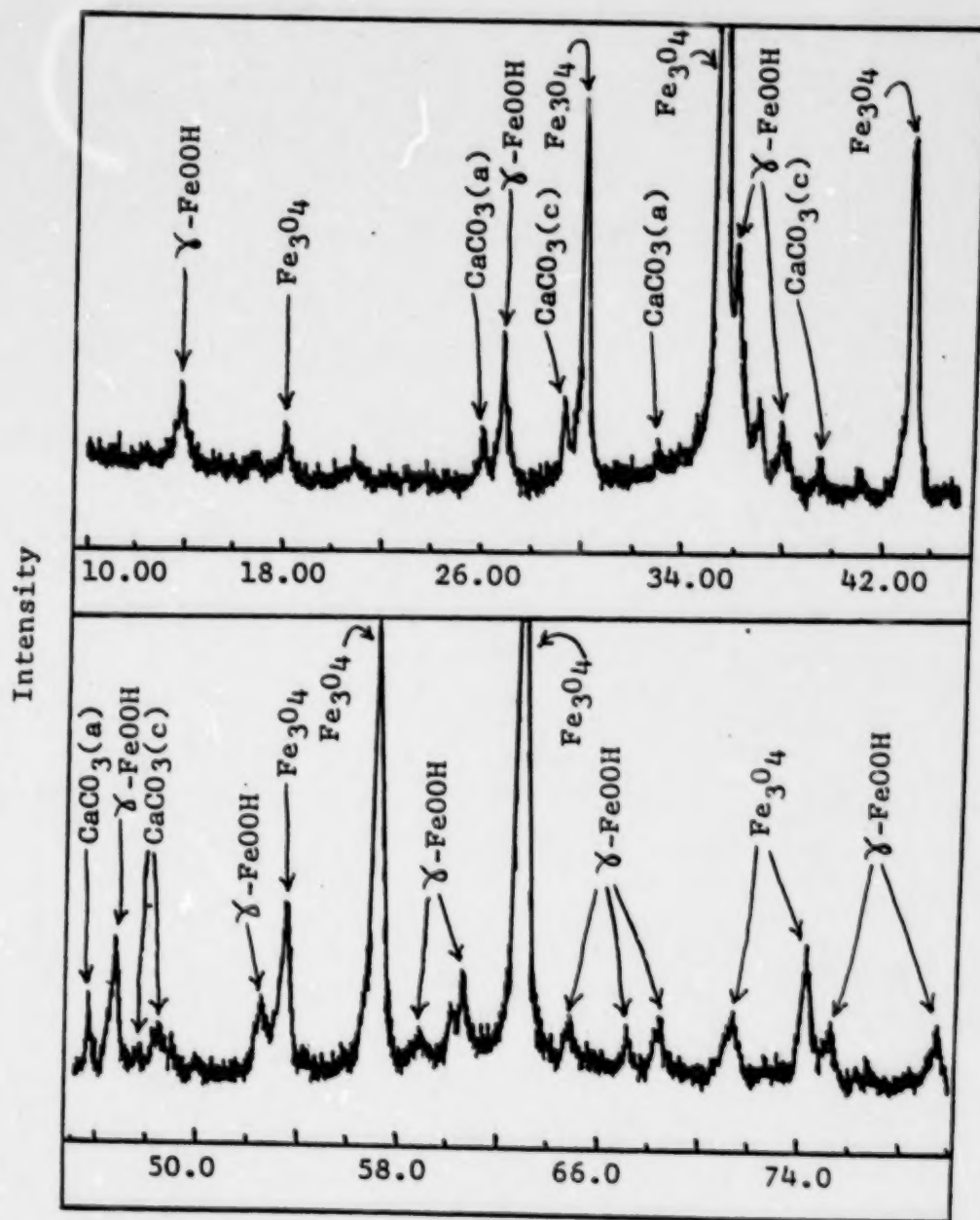


Figure 83. X-Ray Diffractogram of the Corrosion Products of Mild Steel Pipes After 10 Days.

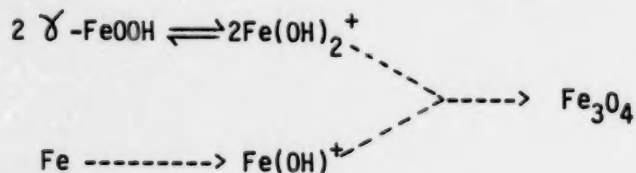


2 θ

Figure 84. X-Ray Diffractogram of the Corrosion Products of Mild Steel Pipes After 20 Days.

CO₃-2, thus exceeding CaCO₃ solubility at the surface.

The X-Ray diffractograms of the corrosion products from black steel pipes are shown in Figures 85, 86, 87, and 88. The dominant peaks in all the graphs were magnetite. Lepidocrocite appeared to be present in scales from waters B, D, and F, but was absent in water E. The peaks for goethite (α -FeOOH) appeared only in corrosion products from water B. Hematite (Fe₂O₃) was absent in scales from waters B, D, and E, but was possibly present in the corrosion products from water F. Aragonite [CaCO₃(a)] appeared to be only present in corrosion products from waters D and E, but both forms of CaCO₃ seemed to be present in the corrosion products of waters B and F. Analysis of iron corrosion products using Mossbauer spectroscopy by other investigators revealed the presence of magnetite, lepidocrocite, goethite, and hematite (150). In addition, Imhoff (151) listed all the forms of hematite, β -, γ -, and α -Fe₂O₃, as having been identified from corrosion products. Feigenbaum *et al.* (152) examined the composition of 15 natural scale layers found in potable water supply mains by X-Ray diffraction and crystalline phase analysis and reported that CaCO₃ was present mostly in the outer zone, while α -FeOOH, FeCO₃, and Fe₃O₄ dominated the inner zone. Siderite (FeCO₃) was not found in the present study even from black steel pipes in contact with waters B and F which had high alkalinity. It is possible that siderite, if ever it existed in the corrosion products, had a poor crystalline form or underwent transformation during the oven-drying of the corrosion products, such that it was not detected during the X-Ray diffraction analysis. The possibility that its solubility product constant had not been exceeded cannot be completely ruled out. Studies conducted by Singer and Stumm (153) showed that FeCO₃ is three times as soluble as would be predicted using the old K_{so} value for siderite. Lepidocrocite has been reported to be the dominant compound present in mild steel corrosion products with α -FeOOH and α -Fe₂O₃ existing in small amounts (145). However, it was found in this study that magnetite appeared as the predominant iron oxide form in the corrosion products. Some of the γ -FeOOH formed initially could have been transformed by one of the two possible mechanisms proposed by Smith and McEnamey (154) for cast iron corrosion products. The first pathway is a dissolution-precipitation reaction in which γ -FeOOH dissociates into Fe(OH)₂⁺ ions which react with FeOH⁺ ions to precipitate as Fe₃O₄.



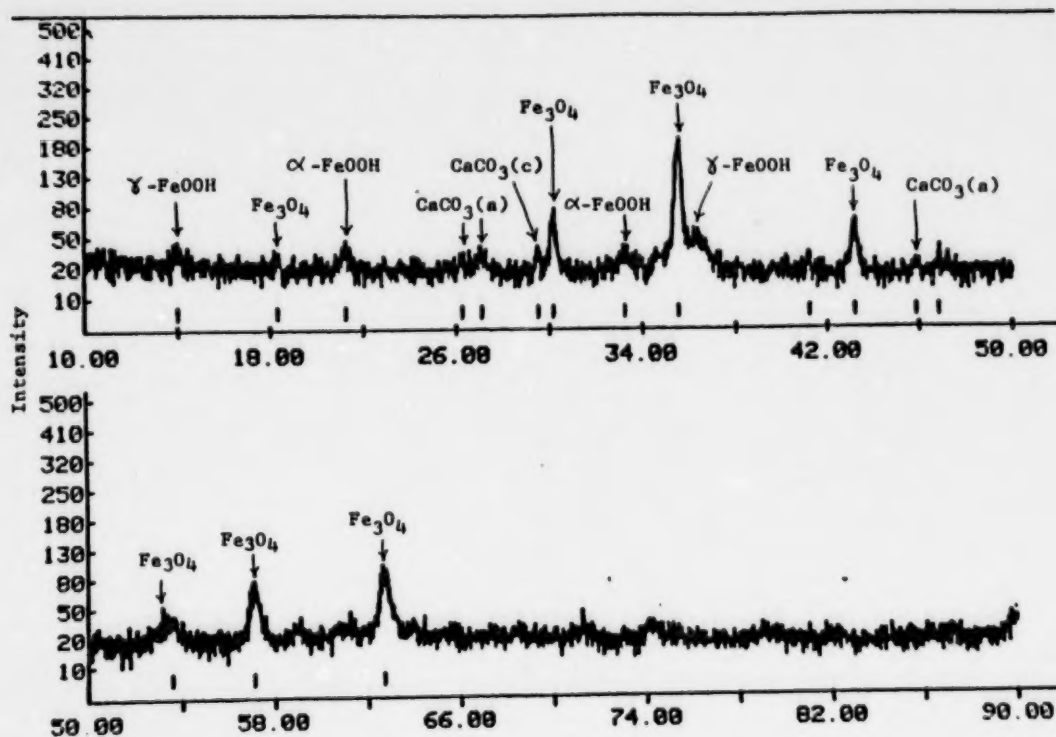


Figure 85. . X-Ray Pattern of Corrosion Products from Black Steel Pipes in Contact with Water B (SI = -0.46).

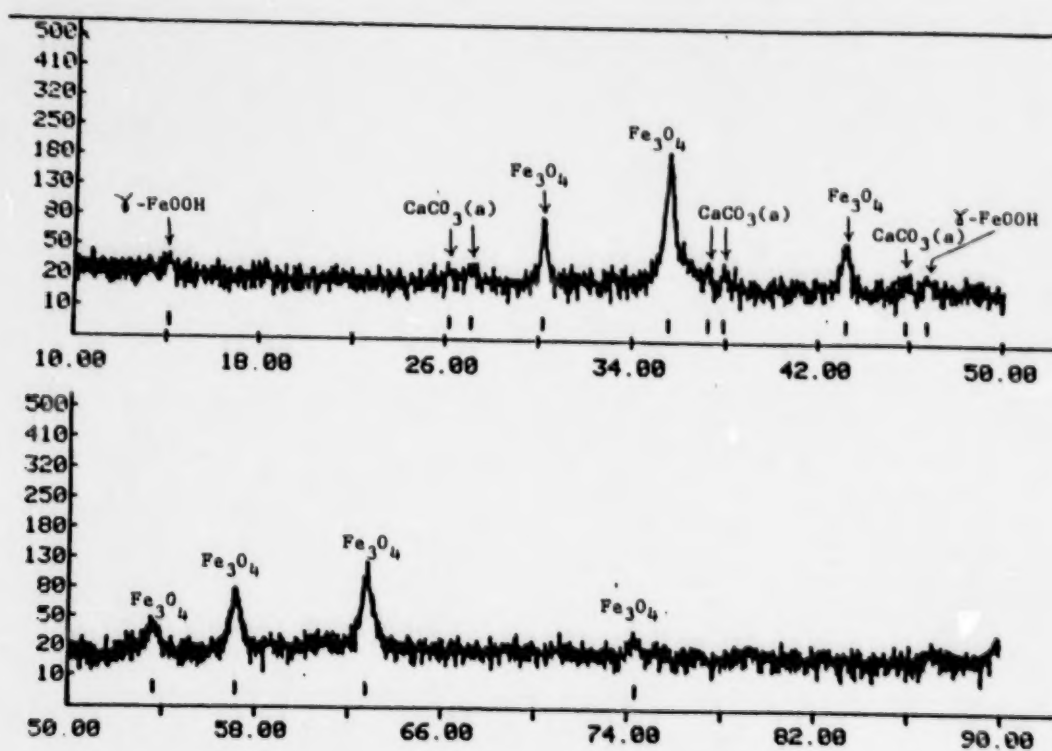


Figure 86. X-Ray Pattern of Corrosion Products from Black Steel Pipes in Contact with Water D (SI = +0.04).

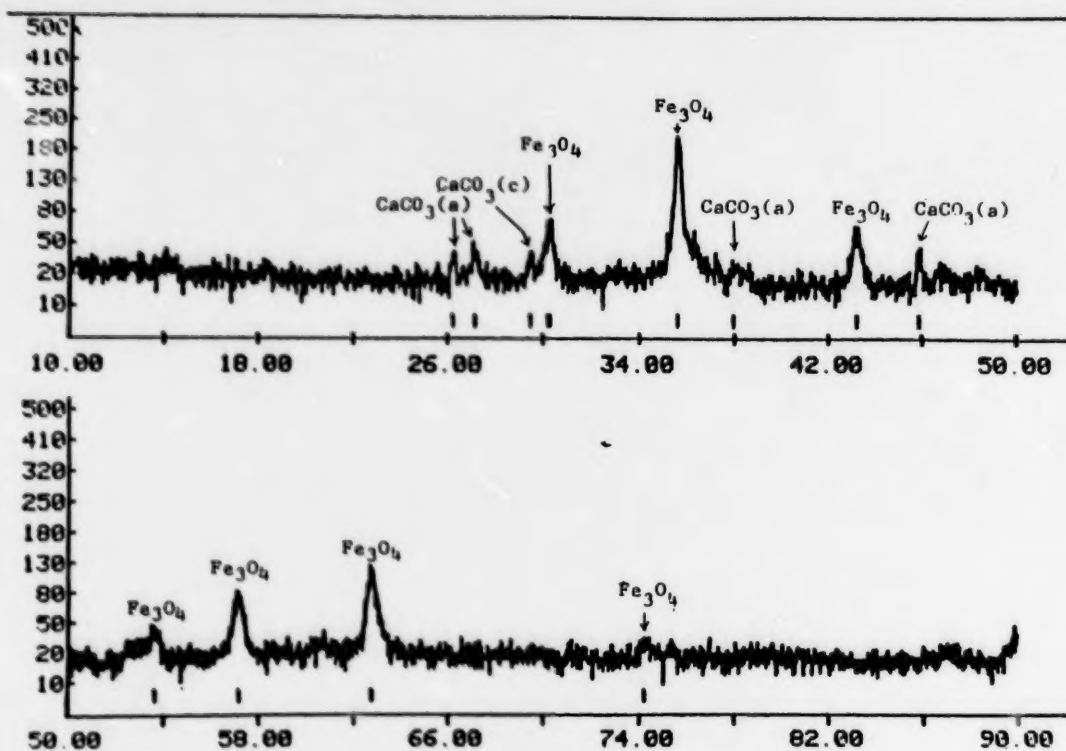


Figure 87. X-Ray Pattern of Corrosion Products from Black Steel Pipes in Contact with Water E (SI = +0.57).

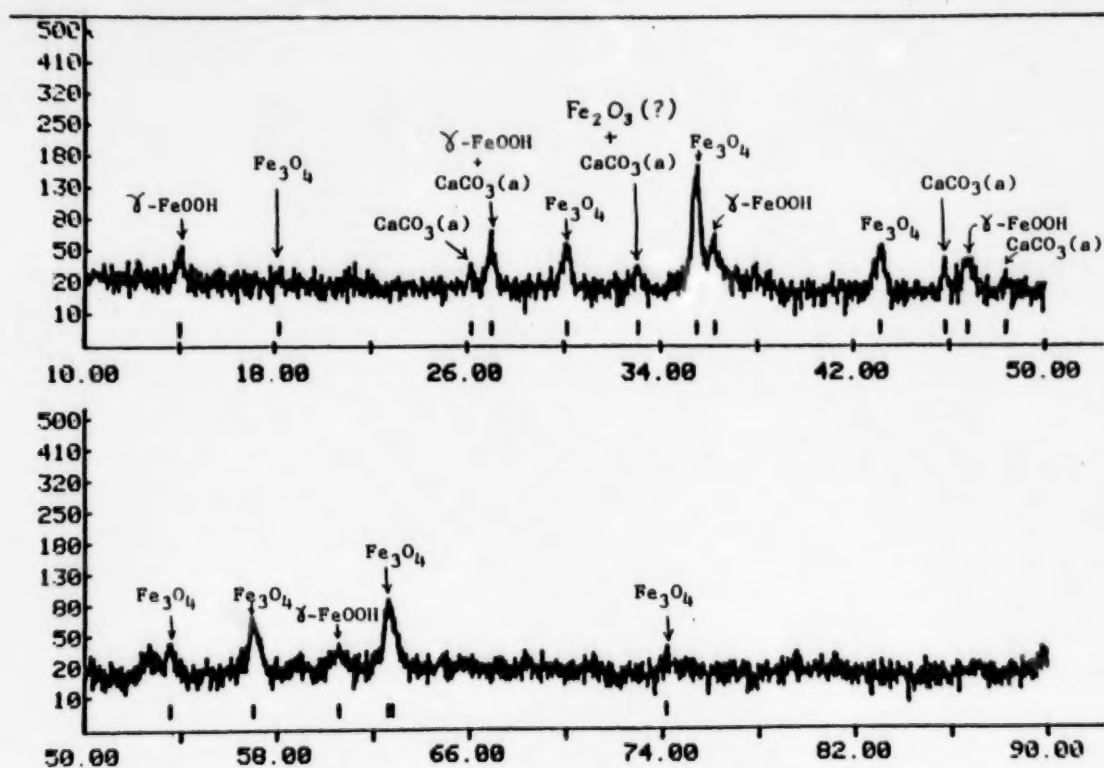
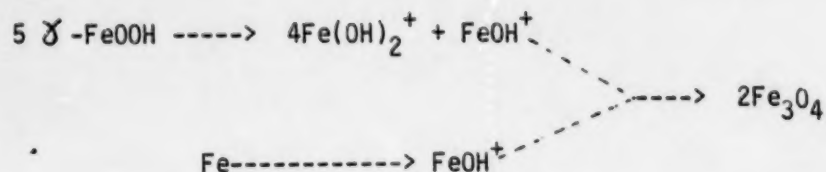


Figure 88. X-Ray Pattern of Corrosion Products from Black Steel Pipes in Contact with Water F (SI = +0.94).

The second is by reductive dissolution in which γ -FeOOH may be dissolved with partial reduction to give both Fe(OH)^+ and Fe(OH)_2^+ ions that react to yield magnetite.



Experimental evidence has been presented for the reductive dissolution of γ -FeOOH (154).

Table 40. Metal Composition of the Corrosion Products from the Black Steel Pipes

Water	SI	Conc. of Fe (% W/W)	Conc. of Ca (% W/W)	Fe/Ca (%) Ratio	Mole Ratio Fe/Ca
B	-0.46	43.2	4.7	9.2	6.57
D	+0.04	47.5	2.7	17.6	12.58
E	+0.57	44.8	9.1	4.9	3.50
F	+0.94	46.5	5.3	8.8	6.28

Chemical analysis was made of the corrosion products from black steel pipes. Table 40 shows the composition of the corrosion products in terms of the amounts of iron and calcium. The concentration of calcium was relatively high in waters E and F with positive SI than those in waters B and D with negative SI. The concentration of iron and calcium varied, respectively, from 43.2 to 47.5% and from 2.7 to 9.1%. These percentages are within the range of values found by Faigenbaum *et al.* (152) from their analysis of the corrosion products collected from potable water distribution systems. Percent Fe varied from 7.2 to 73% and percent Ca ranged from 0.4 to 34%. The percent weight ratio of iron to calcium in this study ranged from 8.8 to 17.6%, while Faigenbaum reported the range $0.2\% < \text{Fe/Ca} (\% \text{W/W}) < 182$. Table 40 shows the range of the Fe/Ca mole ratio in the corrosion products. The highest mole ratio was in water D and the lowest in water E.

Corrosion of Galvanized Steel in Circulating Waters with Different

Saturation Indices

The corrosive behavior of galvanized steel was also studied in the loop system at a flow velocity of 0.38 meter/minute using waters B, D, and E with DO = 5.0 mg/l. The corrosion damage to galvanized steel pipes was evaluated in terms of the weight loss of the metal. Four one-inch metal pipes were used in each experimental run that lasted for 40 days. Figure 89 shows the extent of corrosion of galvanized steel pipes in the bar diagram. The highest corrosion loss was in water B with a negative saturation index. Faster corrosion rate was found in water E than in water D, even though the saturation index of the former was more positive than the latter. Again, it appears difficult to associate increasing positive SI with slower corrosion rates. Other factors are needed to judge the corrosivity of a water toward specific metals. Using the saturation index as the only basis would be too simplistic and could lead to grave errors in evaluating the aggressivity of waters.

Water Quality Changes During Corrosion of Galvanized Steel

Important changes in water quality parameters were monitored at various time intervals during the study period. Only those analytical variables that showed significant changes are listed in Table 41. In all the waters used, calcium concentration and alkalinity exhibited a continuous decline. The rate of decrease of calcium was much faster in waters B and E. There was only a slight decrease of calcium observed in water D. The pH dropped initially and then tended to increase slightly at the end of the 40-day experimental period. As the pH went down, the pHs went up, which explained the shift of the saturation index to increasingly negative values. For instance, water E, with an initial saturation index of +0.53, ended up with a SI = -0.05. The change of buffer capacity with time varied for each water. It increased initially in water B and then started to fall off later. No significant change in β was observed in water D. In water E, it increased for some time and then reverted almost to its initial value. There was a steady increase of dissolved zinc as corrosion progressed. Although the highest corrosion rate occurred in water B, the highest zinc concentration was in water E with the highest conductivity. The change in conductivity with time did not follow the same pattern in the three waters. The conductivity decreased initially in water B but started to climb later. On the other hand, it increased in water D after 5 days. It remained unchanged in water E then began to increase.

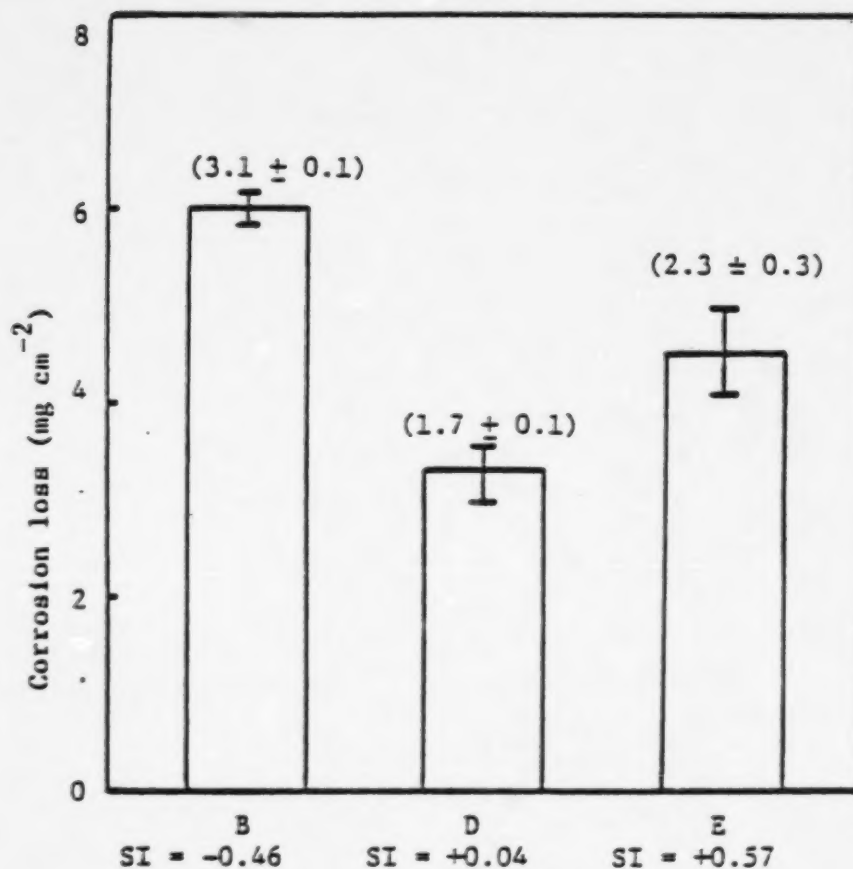


Figure 89. Bar Diagram Indicating the Corrosion Loss from Galvanized Steel Pipes after 40 Days in the Loop System with Circulating Waters of Different Saturation Indices. I Represents $\pm$ One Standard Error. Corrosion Rate in Mils Per Year (mpy) Is Indicated by the Number Inside the Parenthesis Above Each Bar.

Table 41. Water Quality Changes During the Corrosion of Galvanized Steel in Waters with Different SI*

Water	Day	Ca	Alk	Hard	pH	pHs	SI	β	Zn	Cond
B	0	40	148	170	7.25	7.70	-0.45	40	0.00	655
	5	27	135	137	7.05	7.92	-0.87	55	0.02	645
	10	26	125	135	7.00	7.97	-0.97	54	0.06	640
	20	25	126	132	7.05	7.98	-0.93	50	0.10	670
	40	25	120	132	7.10	8.00	-0.90	43	0.12	660
D	0	15	94	99	8.35	8.31	+0.04	5	0.00	400
	5	14	93	96	8.15	8.34	-0.19	5	0.04	420
	10	12	91	92	8.10	8.42	-0.32	5	0.06	415
	20	13	88	94	8.00	8.40	-0.40	6	0.08	400
	40	12	88	92	8.00	8.43	-0.43	6	0.09	390
E	0	120	91	353	8.00	7.47	+0.53	6	0.00	870
	5	103	85	311	7.80	7.56	-0.24	8	0.05	870
	10	97	78	296	7.40	7.63	-0.23	15	0.19	890
	20	94	77	288	7.60	7.65	-0.05	10	0.25	910
	40	92	70	283	7.65	7.70	-0.05	8	0.30	880

* Ca and Zn in mg/l; Alk and Hard in mg/l as CaCO₃; β in mg CaCO₃/l-pH; Cond in μ mho cm⁻¹.

Analysis of Corrosion Products From Galvanized Steel

The decreasing trend of calcium, alkalinity, and pH reflected important chemical events taking place in the solution. As discussed before, localized pH increase in the cathodic areas of the galvanized steel surface could bring about precipitation of calcium carbonate leading to the decrease in calcium concentration and alkalinity. Simultaneously, the zinc ions coming from the corroding metal could precipitate as zinc oxides or hydroxides and possibly zinc carbonate in solutions with greater amounts of free carbonate ions. The quantities of these zinc compounds would be determined by the extent of corrosion, dissolved oxygen concentration, and other chemical factors that affect the ionic interactions in the solution. To gain insight into the nature and identity of the compounds formed during corrosion, the corrosion products from the galvanized steel pipes were analyzed using X-Ray diffraction and atomic absorption spectrophotometry. For comparison, the corrosion products of galvanized steel pipes in contact with deionized water were also subjected to X-Ray diffraction analysis. Figures 90, 91, and 92 show the X-Ray diffractograms of the corrosion products in the deionized water, water B, and water E, respectively. In the deionized water, the major peaks corresponded to two compounds of zinc: zincite (ZnO) and zinc hydroxide [$\text{Zn}(\text{OH})_2$]. There was difficulty in identifying the peaks in the X-Ray patterns for waters B and E. The corrosion products in these waters appeared to contain aragonite [$\text{CaCO}_3(\text{a})$] and possibly hydrozincite [$\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$]. Examination of the corrosion products associated with waters B and E under a polarizing microscope revealed that there were three possible phases, two of which were not well crystallized. The one that was well crystallized appeared to be aragonite. The other phase could have been hydrozincite since most of the peaks in the X-Ray pattern fitted its standard diffractogram. The remaining unidentified phase had a dark orange color which could indicate a compound of iron. Further analysis of a more expanded X-Ray diffractogram (Figure 93) for the corrosion products in water E yielded some additional peaks. Some of these peaks corresponded to those for hematite (Fe_2O_3), especially the strongest line. The presence of hematite or other possible iron oxides was supported by the results of atomic absorption spectrophotometric analysis of a solution of the corrosion products as presented in Table 42. There is, therefore, reason to believe that one of the phases with poor crystalline structure could have been an oxide of iron. During the fabrication of galvanized steel, imperfection could have occurred in coating the steel with zinc such that leaching of iron was made possible during corrosion. This could explain the fact that iron was also detected in the corrosion products for water E. Using Mossbauer spectroscopy, Graham and Cohen (150) examined the corrosion products from galvanized potable water pipes and found $\alpha\text{-FeOOH}$, $\gamma\text{-FeOOH}$, $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 ,

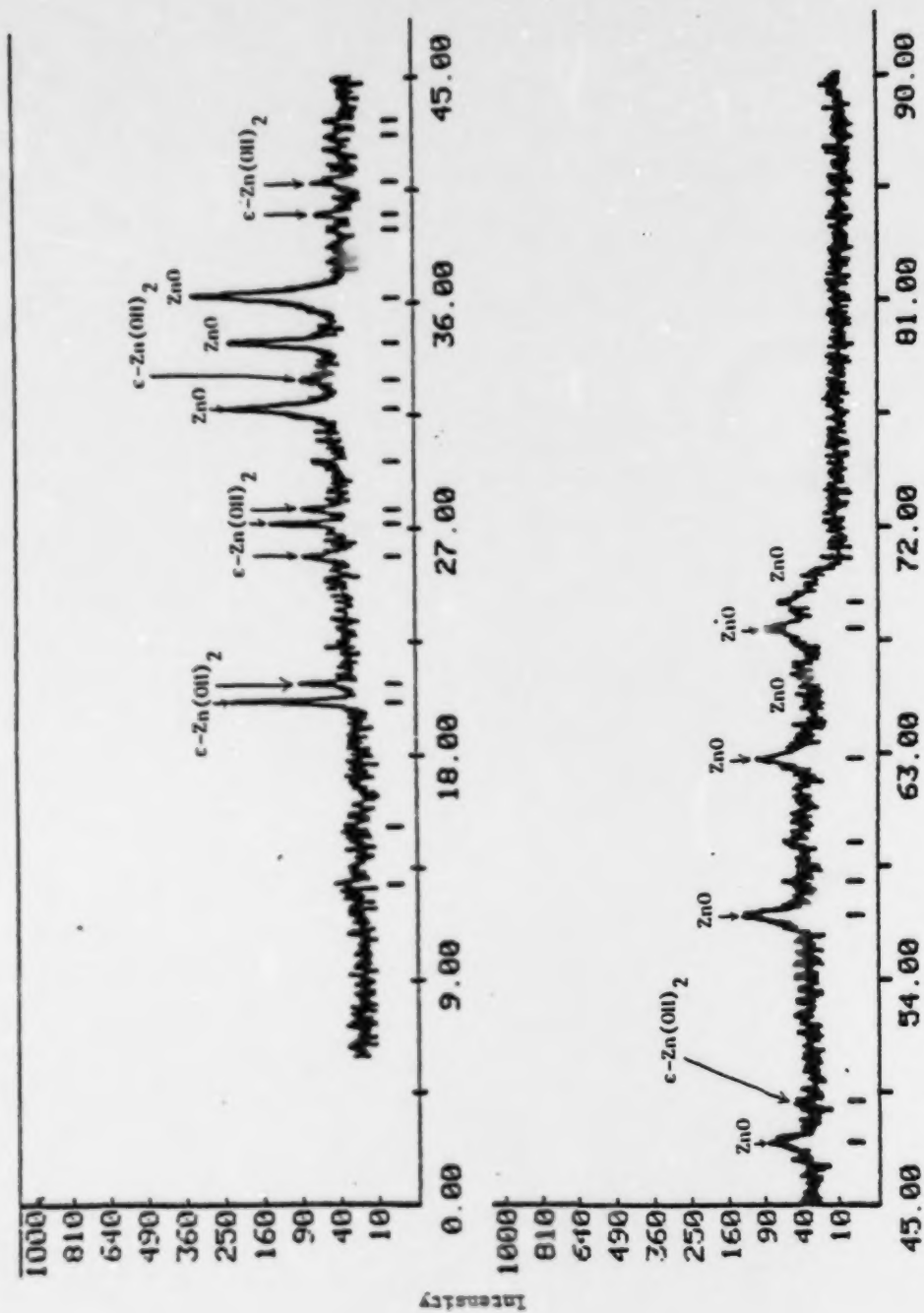


Figure 90. X-Ray Diffractogram of Corrosion Products of Galvanized Steel
In Contact with Deionized Water.

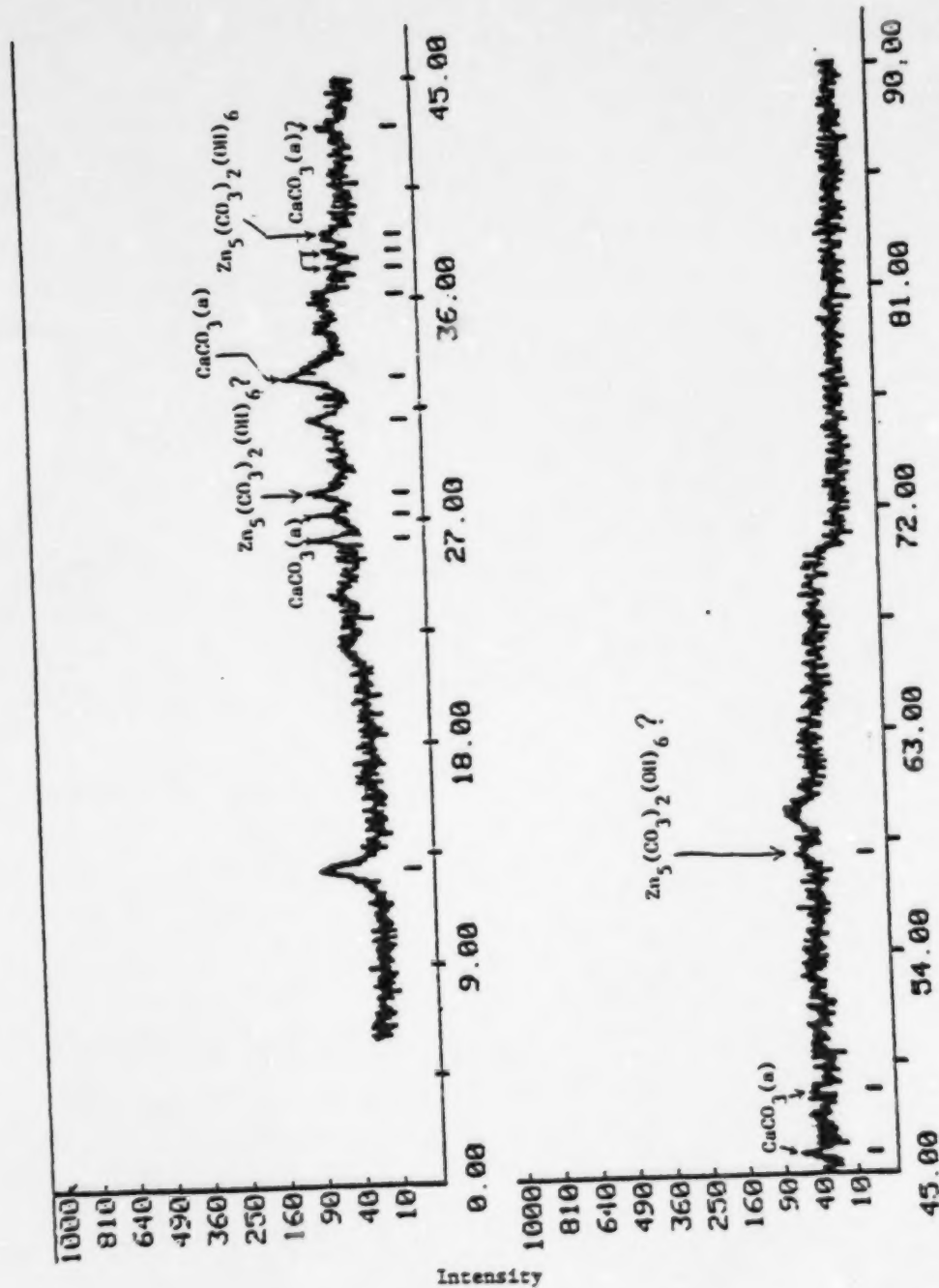


Figure 91. X-Ray Diffractogram of Corrosion Products of Galvanized Steel in Contact with Water B (SI = -0.46).

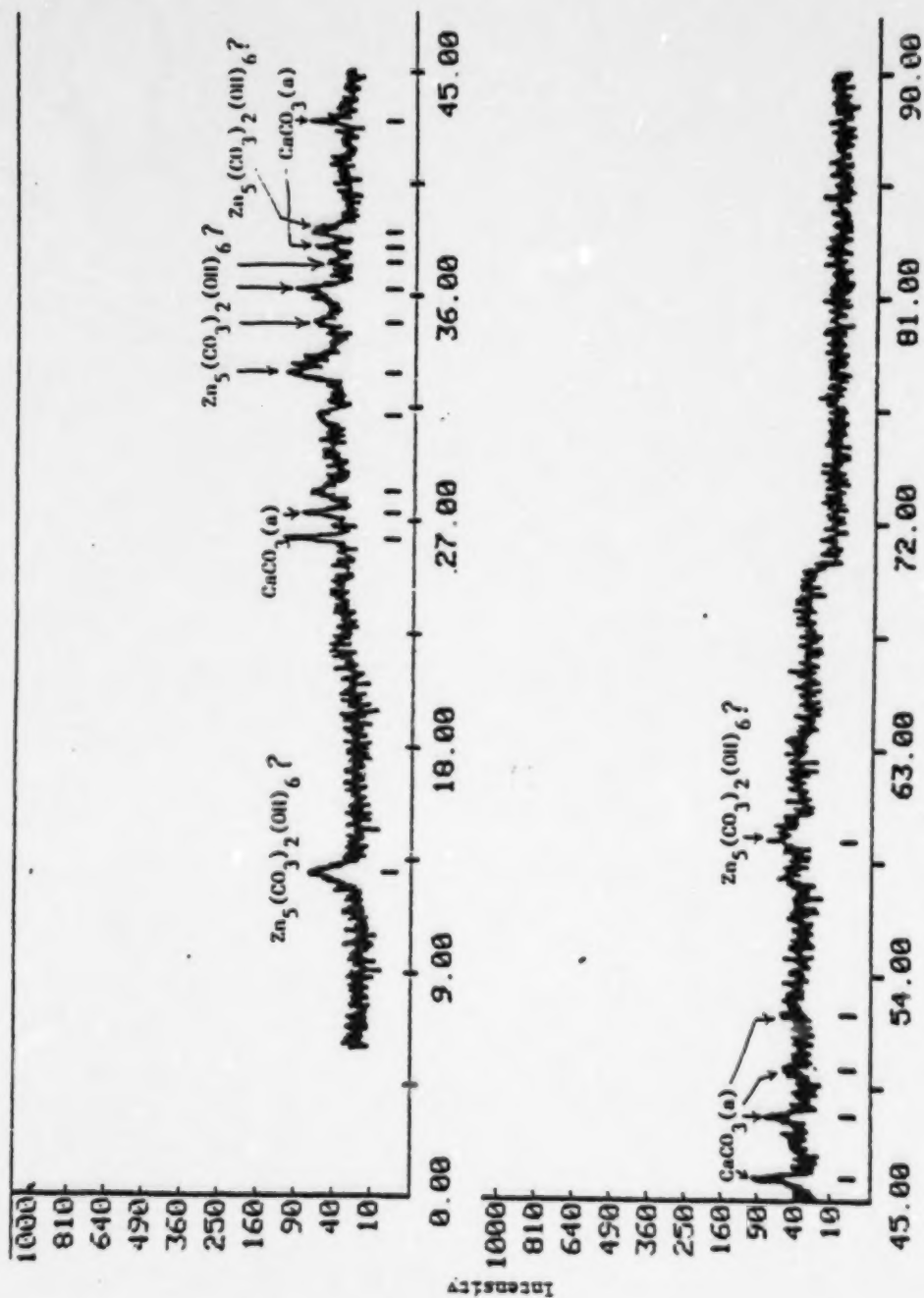


Figure 92. X-Ray Diffractogram of Corrosion Products of Galvanized Steel
In Contact in Water E(SI = +0.57).

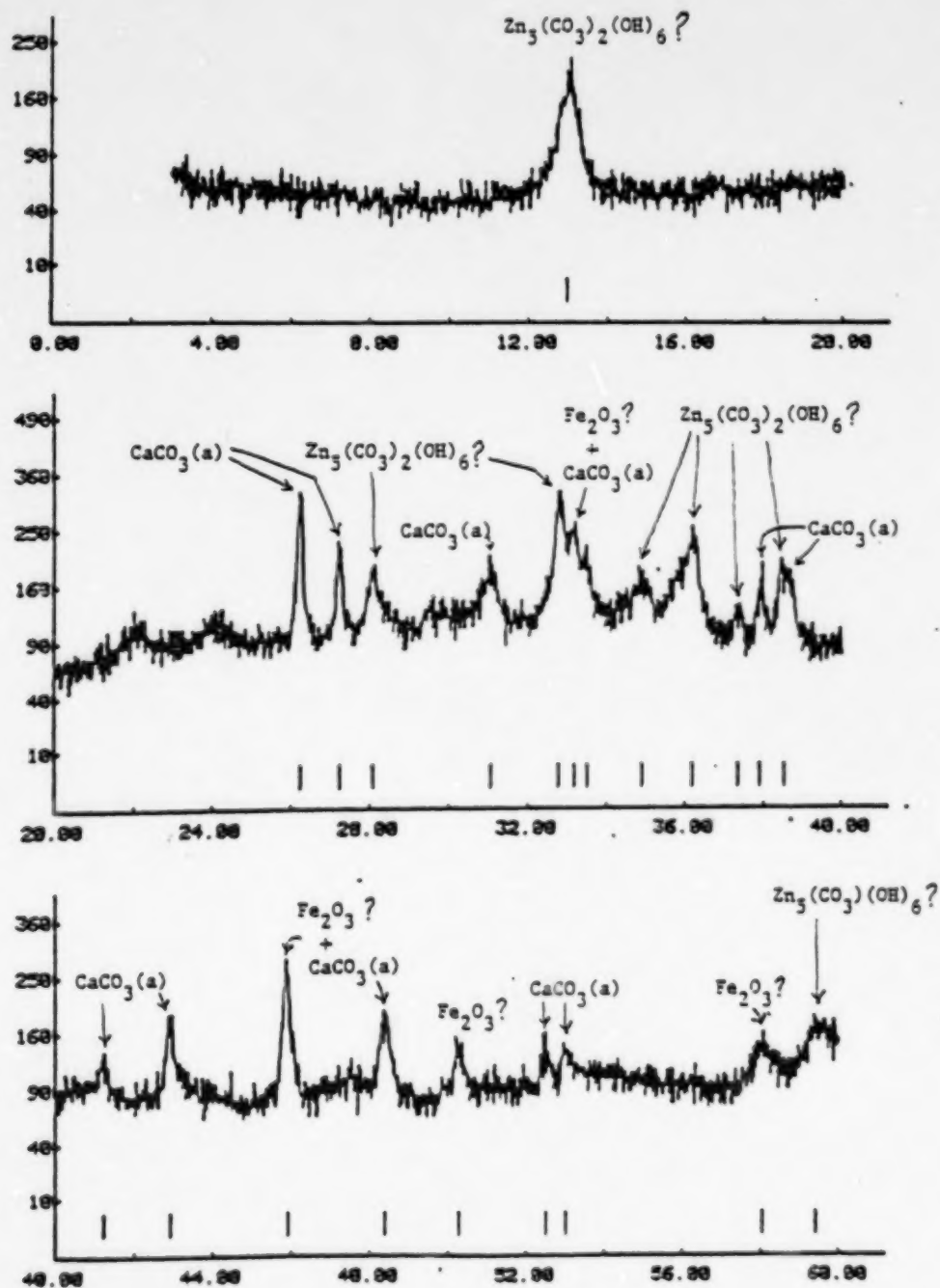


Figure 93. Expanded X-Ray pattern of the corrosion products of galvanized steel in contact with Water E (SI = +0.57).

Table 42. Concentration of the Indicated Metal in the Corrosion Products of Galvanized Steel Pipes

Water	SI	Zn mg g corr. prod.*	Fe mg g corr. prod.	Ca mg g corr. prod.	Cd ug g corr. prod.
B	-0.46	37.1	15.1	7.2	1.8
D	+0.04	39.5	2.2	2.1	2.3
E	+0.57	29.5	4.2	14.3	2.1

* Corrosion product.

and sometimes $Zn_x Fe_{3-x} O_4$. Although zinc and iron were found in the corrosion products under the present study, it was hard to determine whether zinc iron oxide, $Zn_x Fe_{3-x} O_4$, or franklinite, $ZnFe_2O_4$ was present in the corrosion products.

The galvanized steel pipes used in the loop studies have been found to contain cadmium. Table 42 shows the amount of cadmium present in the corrosion products. Although the amount was small, the high toxicity of cadmium to man is a major health concern. Studies conducted by Posselt and Weber (155) on the aqueous chemistry of cadmium indicated that the element could enter drinking waters by corrosion of galvanized steel. They pointed out that under favorable conditions corrosion of cadmium coupled to less noble zinc could proceed at measurable rates in spite of cathodic protection by zinc.

Field Investigation

Four study sites in the distribution system of Florida Water Utilities and three in the South Dade Utilities System were used in the evaluation of the corrosive characteristics of waters flowing through mild steel pipes. Identification of each sampling site for each water utility together with a typical analysis of the water is presented in Table 43. Samples from Florida Water Utilities had a slight tendency to precipitate $CaCO_3$ as indicated by the values of the saturation indices. South Dade Utilities samples were essentially stable with respect to $CaCO_3$ precipitation or dissolution. The alkalinity and concentration of calcium were higher at Florida Water Utilities than at South Dade Utilities. However, the pH levels at the two water utilities were essentially the same.

Both the corrosion rate and pitting index in the two water systems were monitored for almost a year by using the Magna Corrat. A three-electrode Corrat probe was installed at each study site. The changes with time of corrosion rate and pitting index at the sampling locations are illustrated in Figures 94 and 95. At Florida Water and Utilities, higher corrosion rates were observed in the Coral Reef and Kings Bay systems. The Pitting Index was found to be the highest in Kings Bay among the four locations. Generally, the corrosion rates tended to decrease with time. This was found to be the case also at the three sampling sites in the South Dade Utilities System, where the average corrosion rate for the first 20 days was high and then declined. However, the pitting indices showed different trends. At Water Plant No. 1 and Sambo's, the pitting indices initially rose then went down but later began to rise toward the end of the study period. At Water Plant No. 2, it increased initially and then decreased, similar to the trend of the corrosion rate.

Table 43. Typical Analyses of the Waters from the Sampling Points at Florida Water Utilities and South Dade Utilities*

	TDS	Ca	Mg	Na	Cl	SO ₄	Alk	Hard	pH	pls	SI	β
Florida Water Utilities												
Cutler Ridge	264	104	2	14	39	40	215	270	7.19	7.09	+0.10	65
King's Bay	431	114	5	54	110	57	230	305	7.25	7.06	+0.19	62
Coral Reef	184	93	3	14	42	48	200	243	7.20	7.14	+0.06	59
Pine Meadow	268	103	3	11	35	76	225	271	7.06	7.07	-0.01	87
South Dade Utilities												
Water Plant No. 1	298	93	3	17	24	25	221	244	7.10	7.13	-0.03	80
Water Plant No. 2	264	80	3	16	22	31	181	209	7.30	7.27	+0.03	44
Sambo's Water Line	300	93	3	16	22	27	219	244	7.10	7.13	-0.03	79

* All values are in mg/l except Alk and Hard which are expressed in mg/l as CaCO₃. β is in mg CaCO₃/l-phl.

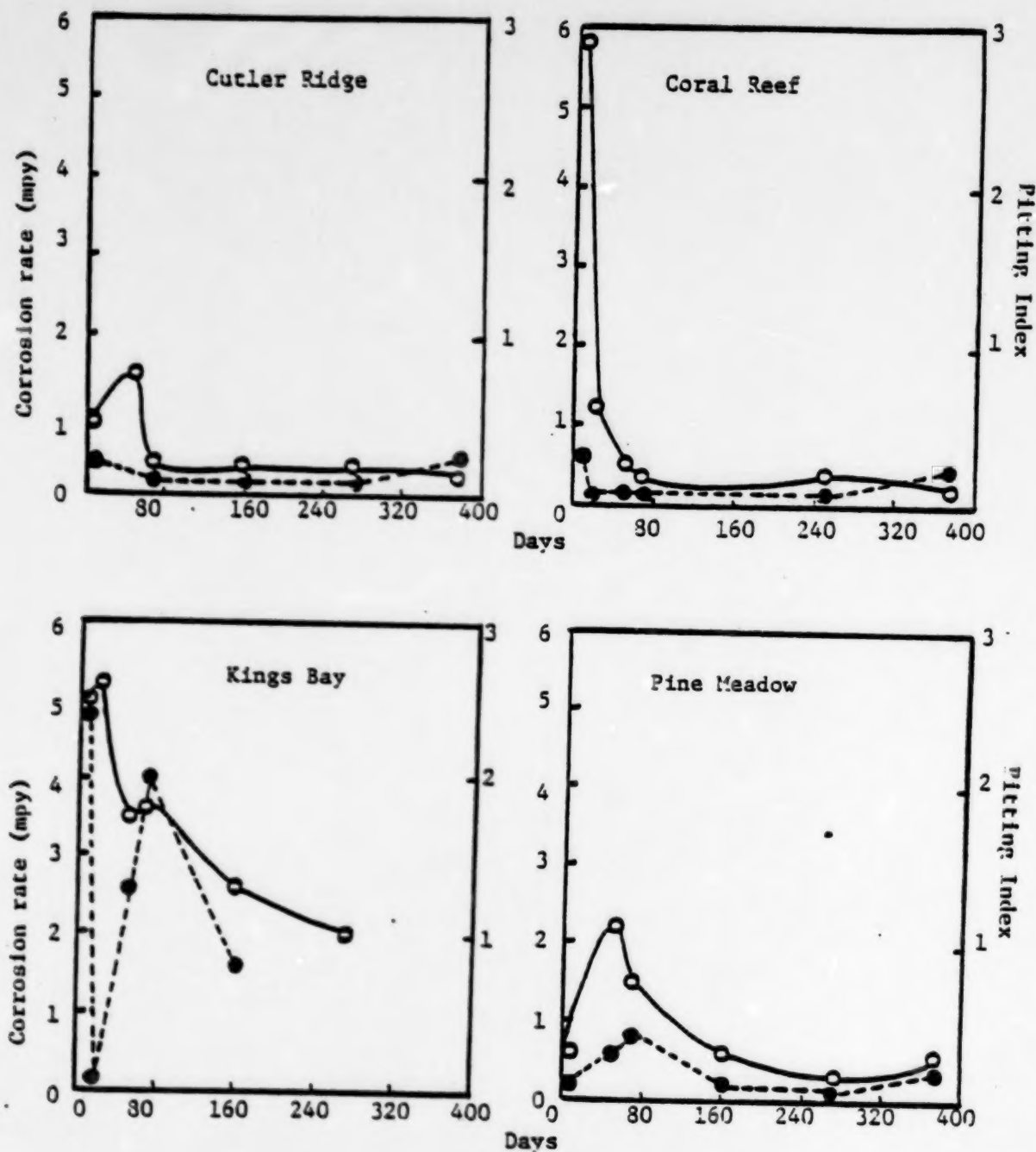


Figure 94. Variation of Corrosion Rate (○) and Pitting Index (●) with Time in Four Sampling Areas in Florida Water Utilities.

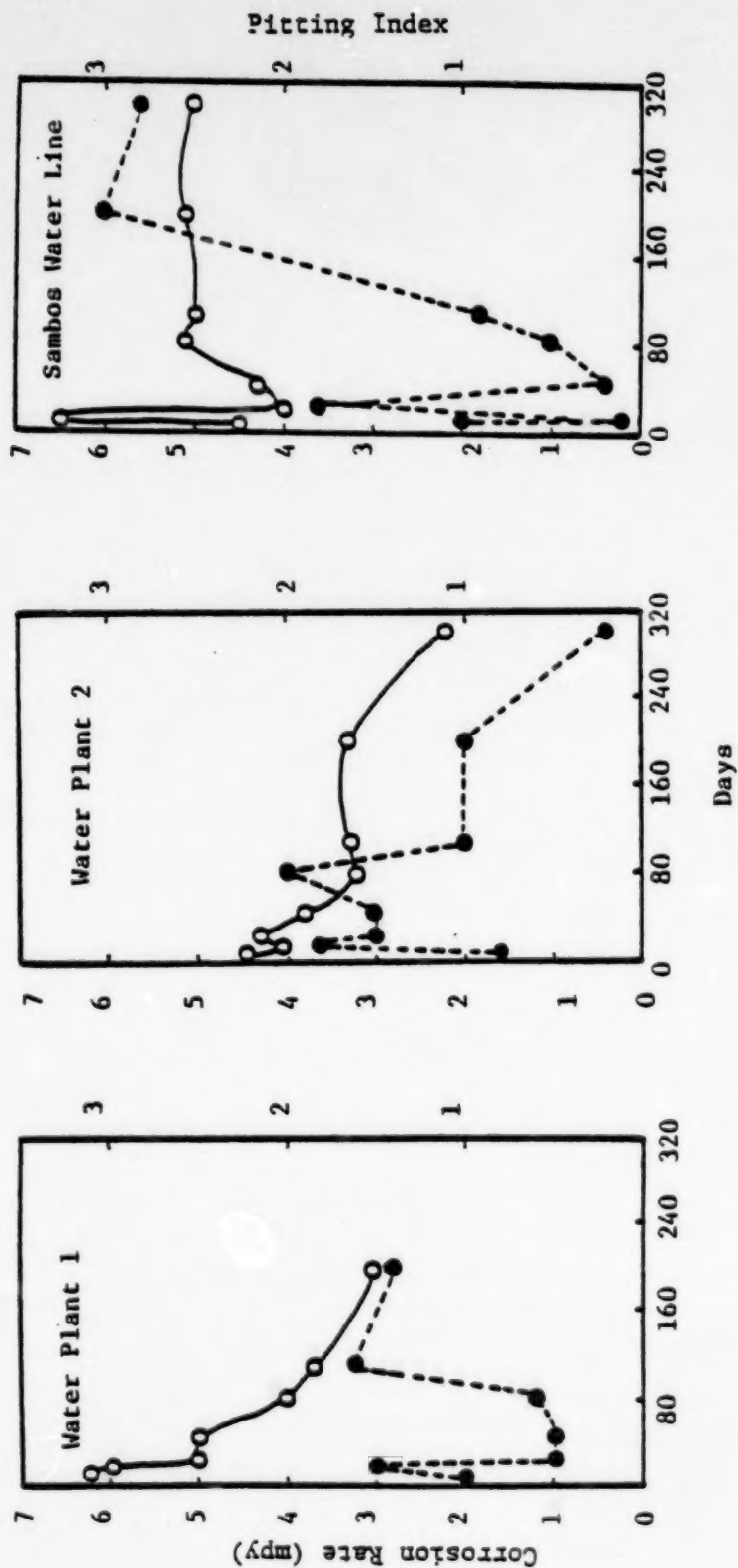


Figure 95. Variation of Corrosion Rate (○) and Pitting Index (●) with Time in Three Sampling Areas in South Dade Utilities.

The summary of results of the corrosion evaluation at the two water utilities is presented in Table 44. The average corrosion rate varied from 0.6 to 4.4 in the Florida Water and Utilities system and from 1.0 to 3.7 in the South Dade Utilities system. The pitting indices ranged from 0.09 to 2.00 at Florida Water and Utilities and from 1.03 to 1.64 at South Dade Utilities. While the overall mean of corrosion rates for Florida Water and Utilities (1.8) and South Dade Utilities (2.1) are comparable, the tendency for pitting at South Dade Utilities was higher. The overall mean of the pitting indices at Florida Water and Utilities was 0.60 compared to 1.29 at South Dade Utilities. The water at either utility was not aggressive to metal pipes since the overall means of the corrosion rates did not exceed 5 mpy, a value that is usually considered as an acceptable or permissible corrosion rate for a protective water. The fact that the water from

Table 44. Average and Standard Deviation of Corrosion Data in Field Studies

Sampling Location	Corrosion Rate (mpy)	Pitting Index
Florida Water and Utilities		
Cutler Ridge	0.6+0.5	0.12+0.08
Kings Bay	4.4+2.0	2.00+1.92
Coral Reef	1.3+0.1	0.09+0.12
Pine Meadow	0.9+0.8	0.18+0.15
Mean	1.8+0.8	0.60+0.55
South Dade Utilities		
Water Plant No. 1	3.7+0.8	1.20+0.55
Water Plant No. 2	1.6+1.5	1.64+1.50
Sambo's Water Line	1.0+0.5	1.03+0.47
Mean	2.1+0.9	1.29+0.84

neither utility showed aggressive properties can be explained by noting the pH, alkalinity, hardness, and buffer capacity in Table 43. It had been observed and experienced by several other investigators (83,84,89) as well as in these studies that waters with high Ca and alkalinity have corrosion-inhibiting properties. At near neutral pH, (pH 7.0 - 7.5) the corrosion rates were found to be lower in the batch experiments using mild

steel in deionized and in Gainesville waters. This could have been due to the higher buffer capacity exerted by the water at this pH. Stumm (89) found that the waters with higher buffer capacities are less corrosive. In the present studies, the buffer capacity at all the sampling sites was sufficiently high such that corrosion appeared to be mitigated.

Correlation of Corrosion Rate of Mild Steel with Saturation

Index and Water Quality Parameters

The results from the laboratory studies of corrosion of mild and black steel confirmed that using the saturation index was inadequate in predicting the corrosive behavior of waters. Other water quality parameters exert important effects on the protective or aggressive properties of waters towards metals. Thus, the correlation between the corrosion rate and other analytical parameters needed to be explored and examined. This could be done graphically, as demonstrated by Ellis (156), or by using statistical methods as was utilized by Haynie and Upham (157) when they analyzed the relationship between the corrosion behavior of steel and atmospheric data.

The correlation studies that will be considered in this section will be limited to mild steel corrosion and water quality data obtained from batch experiments in which 17 test waters were used. There were three levels of dissolved oxygen: low (1.5 ± 0.2 mg/l); medium, (5.0 ± 0.2 mg/l), and high (9.0 ± 0.2 mg/l). The immersion times were 1, 3, 5, and 10 days. The means and range of the water quality parameters for the 17 waters are presented in Table 45. It was felt that the ranges were wide enough to cover most of the analytical parameters that characterize drinking waters. For instance, the saturation index varied from -2.12 to 1.90 and the pH values ranged from 6.70 to 8.95.

The relationship of corrosion rate with each analytical variable was first examined. As illustrated in Figures 96 and 97, the linear correlation of corrosion rate with each separate variable was very weak. There was a scatter of data points and the values of the correlation coefficients demonstrated that corrosion of mild steel under the experimental conditions used could not be expressed in terms of one variable. The plot of corrosion rate against saturation index, SI, tends to show that increasingly positive saturation indices corresponded to relatively lower corrosion rates. The same trend appeared for pH. No apparent trend could be detected in the remaining plots except perhaps in the graph of corrosion rate versus the ratio of alkalinity to the sum of

Table 45. Means and Ranges of Analytical Variables* for the 17 Waters Used in the Batch Corrosion Studies using Mild Steel

Parameter	Mean	Range
TDS	473	116 - 791
Ca	68	10 - 120
Mg	16	2 - 52
Na	64	7 - 130
Cl	119	18 - 213
SO ₄	79	16 - 208
Alkalinity, mg/L as CaCO ₃	116	21 - 232
β (mg/L as CaCO ₃ /pH)	16	3 - 42
pH, units	7.77	6.70 - 8.95
pHs, units	7.79	7.60 - 9.07
Saturation Index, units	-0.02	-2.12 - +1.90
Conductivity, umho-cm-1	696	165 - 1370
Ionic strength, moles/L	0.0081	0.0001 - 0.0198
Dissolved Oxygen	5.1	1.4 - 9.1
Time, days	5	1 - 10

*All values are expressed in mg/L except as indicated.

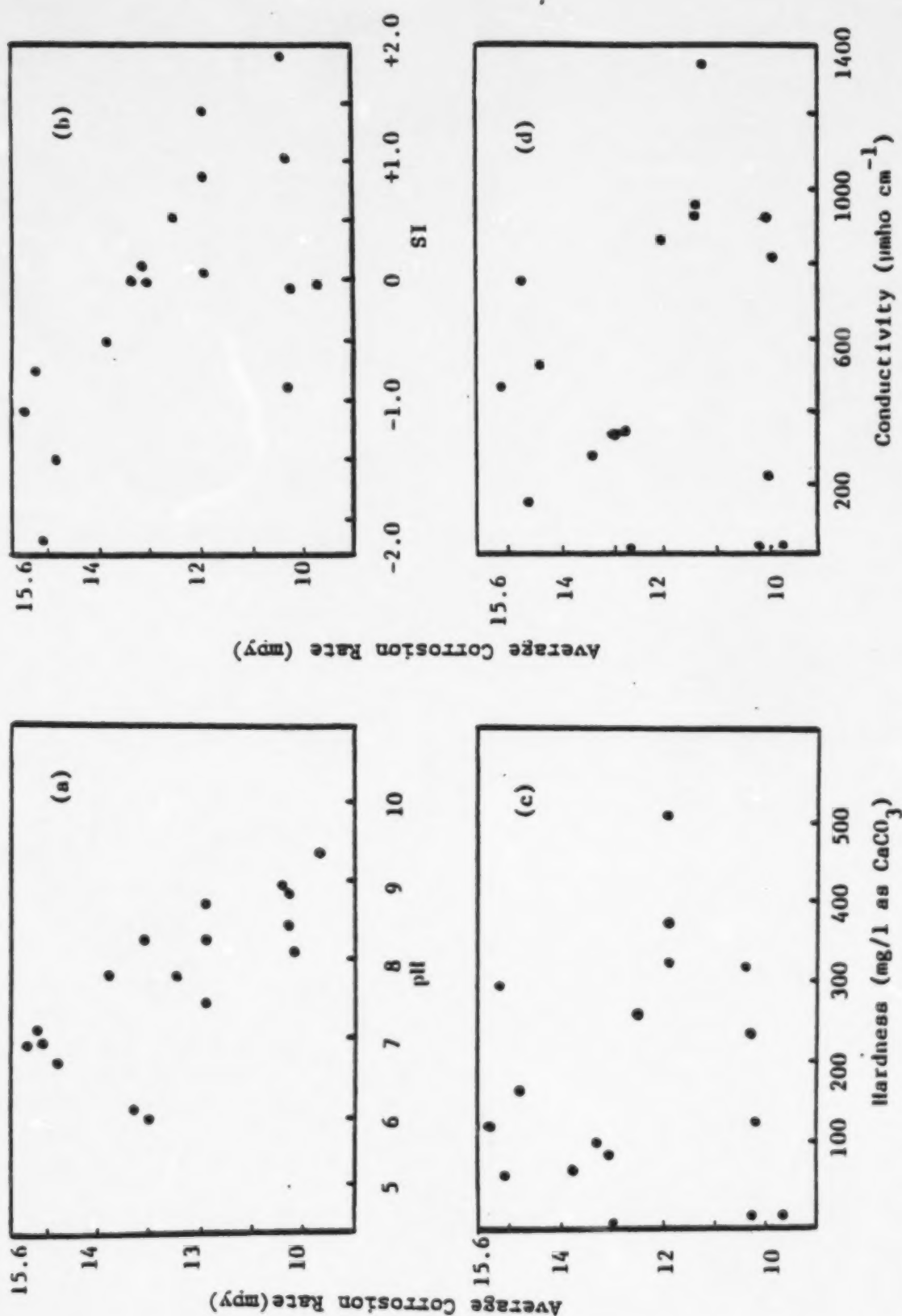


Figure 96. Plots of the Ten-Day Average Corrosion Rate of Mild Steel against (a) pH, (b) Saturation Index, (c) Hardness, and (d) Conductivity. The Data are from the Jar Corrosion Experiments involving 17 Waters.

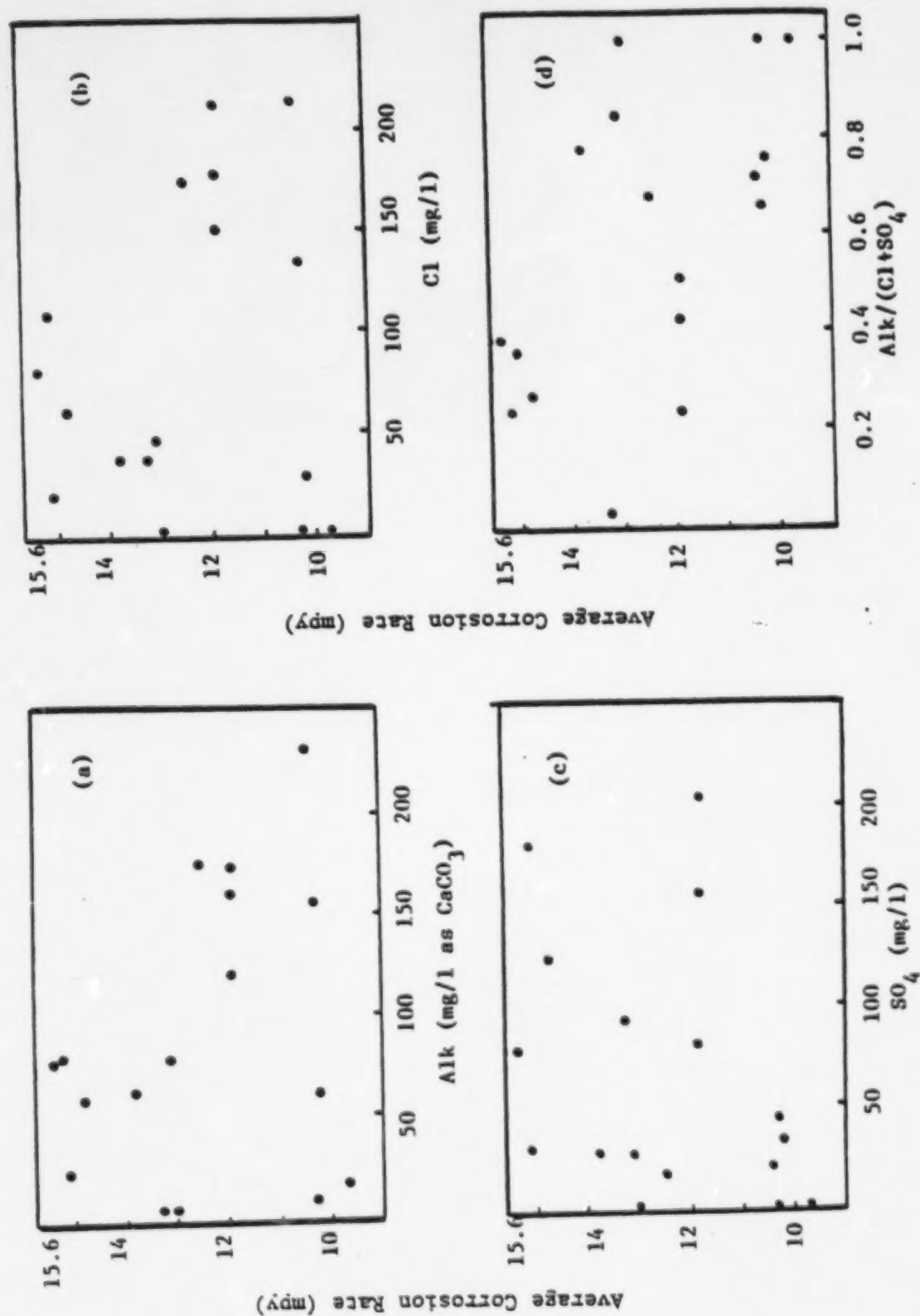


Figure 97. Plots of the Ten-Day Average Corrosion Rate of Mild Steel against (a) Alkalinity, (b) Chloride, (c) Sulfate, and (d) Equivalent Ratio of Alkalinity to the Sum of Chloride and Sulfate. The Data are from the Jar Corrosion Experiments Involving 17 Waters.

chloride and sulfate. Generally data points corresponding to higher ratios appeared to inhibit corrosion implying that increasing the alkalinity, while the chloride and sulfate concentrations remain constant, would make the water more protective rather than aggressive. On the contrary, holding the alkalinity constant while increasing the amounts of chloride and sulfate would be expected to promote corrosion.

An empirical mathematical model for corrosion rate was hypothesized:

$$\text{Corrosion Rate (CR)} = (\text{Cl})^{\alpha_1} (\text{SO}_4)^{\alpha_2} (\text{DO})^{\alpha_3} (\text{Alk})^{\alpha_4} (\text{Ca})^{\alpha_5} (10^{\text{SI}})^{\alpha_6} (\beta)^{\alpha_7} (\text{time}_d)^{\alpha_8}$$

After linearizing the model by log transformation, a multiple linear regression analysis was performed using the Statistical Analysis System (SAS) method. The squared multiple correlation coefficient, R^2 , was evaluated and found to be 0.983. This indicates that the logarithmic model could account for 98 percent of the variation in corrosion rate. The equation was then transformed back into its original nonlinear form with the regression coefficients

$$\text{CR} = \frac{(\text{Cl})^{0.509} (\text{SO}_4)^{0.025} (\text{Alk})^{0.423} (\text{DO})^{0.799}}{(\text{Ca})^{0.676} (\beta)^{0.030} (10^{\text{SI}})^{0.107} (\text{Day})^{0.381}}$$

Using this predictive equation, the corrosion rates of mild steel in the jar tests were computed. Figure 98 shows the graphical comparison between the observed and predicted values. Despite some scatter of data points, a satisfactory fit of data was obtained.

The eight-variable predictive model suggests that increasing the chloride, sulfate, alkalinity, and dissolved oxygen would accelerate corrosion, whereas increase in calcium, buffer capacity, saturation index, and exposure would result in lower corrosion rate. The model further implies that when the saturation index is negative, the corrosion rate would be faster assuming the other variables do not change. Conversely, water with a positive saturation index would be expected to reduce the corrosion rate if the other variables remain constant. But the entire extent of corrosivity will be determined by considering, in addition to saturation index, corrosion-promoting substances such as chloride, sulfate, and dissolved oxygen, and corrosion-inhibiting agents like calcium and buffer capacity. Unexpectedly, alkalinity appears in the predictive equation to be an accelerating factor. This could be due to the

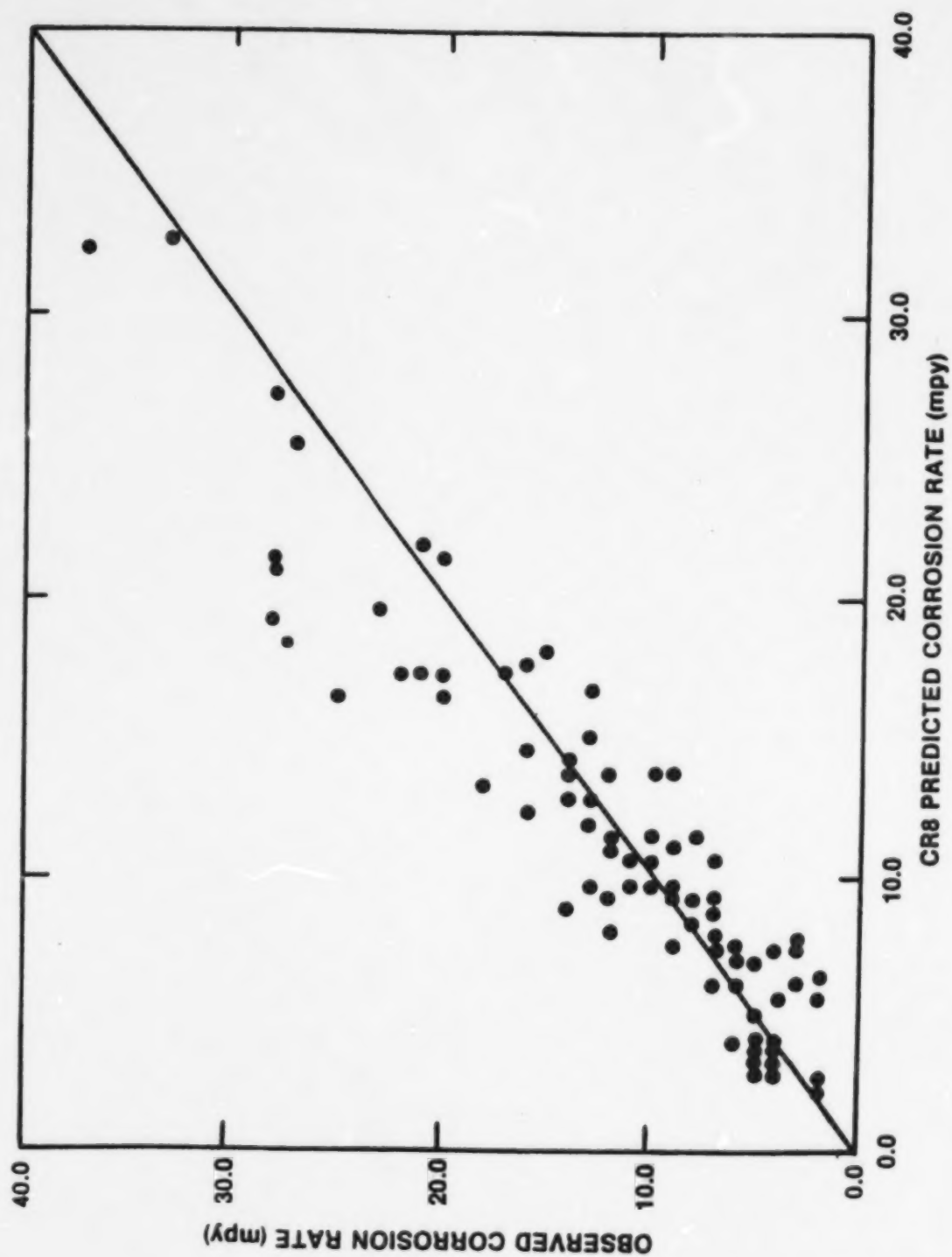


Figure 98. Comparison of Observed and Predicted Values from the Eight-Variable Mathematical Model (CR8).

masking effect rendered by increasing conductivity when the alkalinity of the test solutions were being raised by adding NaHCO_3 which simultaneously increased the ionic strength. In other words, there could be a point reached when the inhibitive influence of alkalinity could be overwhelmed by the ionic conductivity which favors corrosion.

Additional statistical tests were performed. Using the General Linear Model (GLM) procedure of SAS, other predictive corrosion rate models with and without intercepts were constructed. Preliminary analysis showed that models with constant terms gave lower R^2 values than those with no intercepts. Therefore, statistical analyses were later confined to testing models without intercepts. Some of the best models are presented in Table 46 including the empirically formulated model discussed previously. The first predictive equation, which is a linear combination of five variables could account for 90% of the variability in corrosion rate. The variance in corrosion rate could be explained by the changes in total calcium, dissolved oxygen, buffer capacity, pHs, and immersion time. However, a poor graphical fit was obtained with this equation. Predictive models described by equations 2 to 5 are all expressed in logarithmic functions and were much better in that 98 to 98.5% of the variance in corrosion rate could be accounted for. The second and third models can be also written as follows:

$$\text{CR4T} = \frac{(\text{TDS})^{0.253} (\text{DO})^{0.820}}{(10^{\text{SI}})^{0.087} (\text{Day})^{0.373}}$$

$$\text{CR4C} = \frac{(\text{Cond})^{0.238} (\text{DO})^{0.822}}{(10^{\text{SI}})^{0.086} (\text{Day})^{0.371}}$$

Thus, either TDS or conductivity (Cond) could be used with dissolved oxygen, saturation index, and exposure time to estimate corrosion rate. This is so because essentially all of the dissolved solids are in form of ionic solutes whose total concentration affects the conductivity of the solution.

Addition of other water quality factors did not improve much the fit of the predictive equations to the data. Models 4 and 5 yielded R^2 values of

Table 46. Mathematical Models for Predicting Corrosion Rate.

Predictive Equation	R ²
1. $CR = -0.016 Ca + 0.073 B + 1.719 DO - 1.299 Day + 1.178 pHs$	0.901
2. $\log CR_{4T} = 0.253 \log(TDS) + 0.820 \log(DO) - 0.0876 \log(10^{SI}) - 0.373 \log(Day)$	0.982
3. $\log CR_{4C} = 0.238 \log(Cond) + 0.822 \log(DO) - 0.862 \log(10^{SI}) - 0.371 \log(Day)$	0.981
4. $\log CR_{4C} = 0.509 \log(Cl) + 0.0249 \log(SO_4) + 0.423 \log(Alk) + 0.780 \log(DO) - 0.676 \log(Ca) - 0.0304 \log(\beta) - 0.381 \log(Day) - 0.107 \log(10^{SI})$	0.984
5. $\log CR_{14} = 0.221 \log(Ca) + 1.178 \log(Mg) + 0.363 \log(Na) + 6.552 \log(Cl) + 0.364 \log(SO_4) + 4.179 \log(Alk) + 0.053 \log(\beta) + 0.784 \log(DO) + 21.232 \log(pHs) + 0.150 \log(10^{SI}) - 5.605 \log(TDS) - 13.350 \log(pH) - 5.681 \log(Cond) - 0.382 \log(Day)$	0.985

0.984 and 0.985, respectively. Actually, some of the variables in these models are not truly independent. Calcium and alkalinity are related to SI while pH and alkalinity determine buffer capacity. Hence, the four-variable models could then be used for predicting corrosion rates under the test conditions employed in this study. In particular, the CR4T equation was chosen because the parameter TDS is more commonly reported than is conductivity.

When the CR4T model was graphically fitted to the observed data, the resulting plot in Figure 99, shows a striking similarity with that for CR8 model shown in Figure 98. This implies that this CR4T model is as good as the empirically developed model. To assess further the reliability and accuracy of the CR4T model, the observed corrosion rates after 1, 3, 5, and 10 days of waters e, k, and q, were superimposed on the predicted corrosion time curves. Figure 100 shows the prediction curves for the three waters tested with 5.0 ± 0.2 and 9.0 ± 0.2 mg/L dissolved oxygen. Most of the experimental data points lie close to the curve. The observed values follow a decreasing trend with time as with the predicted corrosion-time curves.

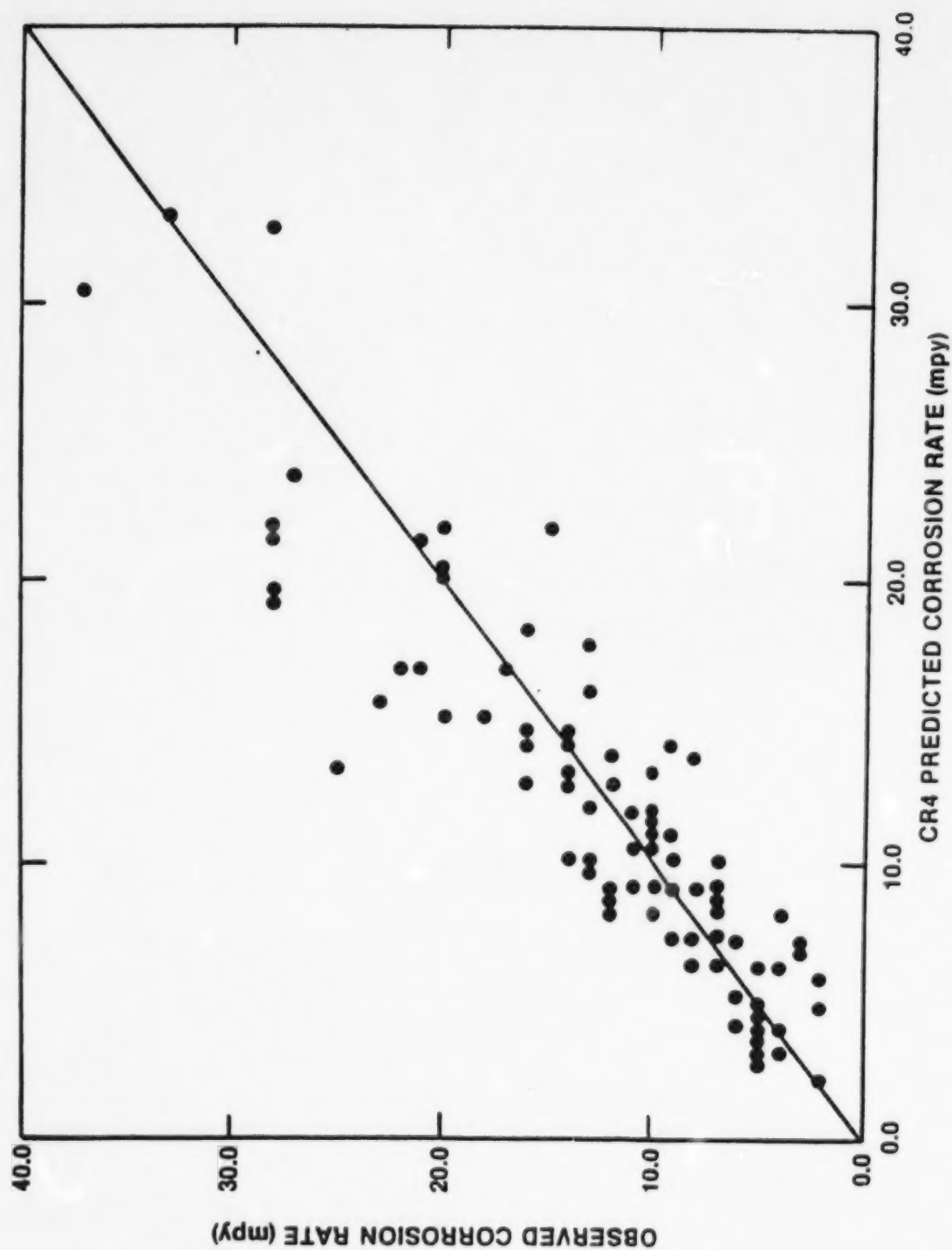


Figure 99. Comparison of Observed and Predicted Values from the Four-Variable Mathematical Model (CR4T).

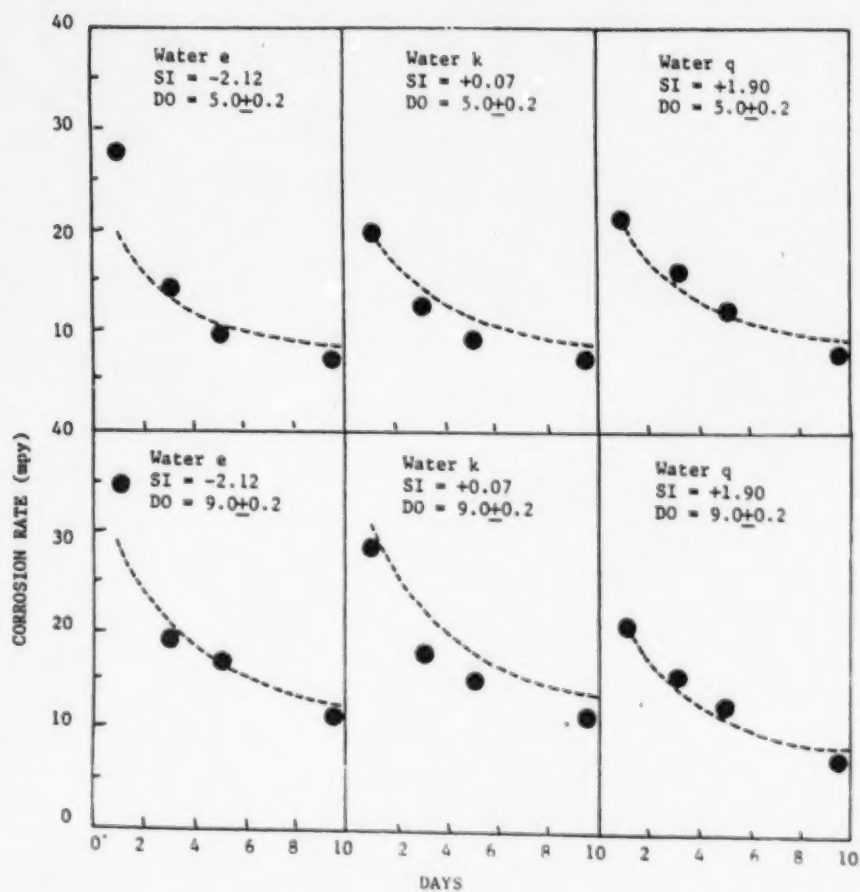


Figure 100. CR4T-Predicted Corrosion-Time Curves (---) and Experimental Values (●) for Mild Steel in Waters e, k, and q.

SECTION 9

SUMMARY

Studies of corrosion are important, not only from the standpoint of understanding the processes but also in controlling it. Several corrosion indices have been proposed to assess the aggressive properties of the potable waters towards the metallic structures in distribution systems. The most popular and widely used is the Langelier Saturation Index which is calculated by determining the actual pH and pHs or theoretical pH at which the water is saturated with CaCO_3 . Langelier's equation for pHs has been shown not to be sufficiently accurate. Several statistical models were developed based on data from 155 water samples, to find a simpler equation for accurately predicting the pHs value obtained from exact calculations of the pHs using all relevant equilibrium equations and requiring the use of a computer.

A five-variable prediction model was developed which had an $R^2=0.98$. The model was logarithmic and required that, the total dissolved solids and total (analytical) concentrations of calcium, magnesium, alkalinity and sulfate be known at a given temperature. Comparison with other predictive models was made as well as with several of the computer models for exact calculations.

Experiments utilizing weight loss and electrokinetic measurements for corrosion rates were conducted in batch and loop systems. Synthetic waters with different saturation indices pH, buffer capacity, dissolved O_2 , chlorine residual, color, and varying amounts of major cations and ions were used in these experiments. The effects of different water quality parameters on the corrosion rates of mild steel, galvanized steel, and copper were similarly studied. Pourbaix diagrams were constructed for some metal-aqueous systems and experimental Eh values were compared to these equilibrium potential-pH graphs. Field investigation of corrosion rates and pitting indices were carried out in selected test locations in Florida. The corrosion products from steel specimens in the loop studies were analyzed using the automated X-Ray Powder Diffractometer and wet chemical techniques. Predictive equations for corrosion rate were developed from the corrosion data on mild steel using multivariate statistical analyses.

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